Author:
Murguia Flores, Fabiola

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Modelling the global atmospheric methane uptake by soils in the past, present and future

Modelling the global atmospheric methane uptake by soils in the past, present and future

Fabiola Murguía Flores

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Abstract

Soil bacteria known as methanotrophs are the only biological sink for atmospheric methane (CH_4). Soil methanotrophy is controlled by a plethora of factors, including temperature, soil texture, moisture and nitrogen inputs, resulting in spatially and temporally heterogeneous rates of soil methanotrophy across the globe. As a consequence, the exact magnitude of the global soil sink, its temporal and spatial variability and the attribution of the main drivers of change, remain poorly constrained. For this reason, a new model to estimate global atmospheric CH_4 uptake by the soil MeMo (Methanotrophy Model) was developed by introducing several advances (*i.e* the effect of N input via fertilizers) to previous existing models in the light of recent findings. The improved structural and parametrical representation of key drivers of soil methanotrophy in MeMo results in a better fit to observational data in a latitudinal distribution comparison with previous models, representing the first validation of global methanotrophy models. MeMo was then employed to simulate and quantify the uptake of atmospheric CH_4 by soils at the global scale through different time periods. The new model runs showed a constant increase in global CH_4 uptake since the last glacial maximum to the preindustrial era (from 7 to 17 Tg CH_4 y^{-1}), a sharp increase in the last 100 years (from 17-35 Tg CH_4 y^{-1}) and likely increase in the future, depending on the scenario (from 23-89 Tg CH_4 y^{-1}). The changes were further attributed to fluctuations in atmospheric CH_4 concentration during the paleo-record and the last century, however in recent decades temperature and nitrogen inputs started to have a larger influence on regional trends which are likely to be more pronounced in future RCPs.

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Finally, I would like to dedicate this work to the memory of my father, whose love for me and for knowledge made me love science. ¡Gracias Papá!

Author’s declaration

I declare that the work in this dissertation was carried out in accordance with the requirements of the University's *Regulations and Code of Practice for Research Degree Programmes* and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate's own work. Work done in collaboration with, or with the assistance of, others, is indicated as such. Any views expressed in the dissertation are those of the author.

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Table of contents

List of figures

List of tables

CHAPTER 1

Introduction

1.1 The global methane cycle

Methane (CH_4) is the most abundant organic gas in the Earth´s atmosphere, one of the most potent greenhouse gases and the second contributor to human-induced climatic change. CH_4 has a Global Warming Potential (GWP) that is 28 times larger than CO_2 and it is responsible for 20% of the global warming caused by all greenhouse gases so far (Myhre et al., 1998; Ciais et al., 2013). However, CH_4 has a short atmospheric life time of 9±2 years, thus making it an ideal target for climate change mitigation (Saunois et al. 2016).

Since the last glacial maximum (about 21,000 years ago), the concentration of CH_4 in the atmosphere increased from 375 to 722 ppb until the preindustrial era. Over the last 300 years, the concentration of atmospheric CH_4 increased from 722 to 1800 ppb due to changes in human activities and land use change, while the last 30 years have seen an increase of 0.8 to 1.0% per year (Kirschke et al., 2013; IPCC 2014). According to different representative concentration pathways (RCP) proposed by IPCC (Taylor, 2012), the atmospheric CH_4 concentration could reach a maximum of 3600 ppb by the end of 2100 in RCP8.5 or decrease to a minimum of 1200 ppb in RCP2.6 scenario.

CH_4 originates from both non-biogenic and biogenic sources. Biogenic sources account for almost 60% of the total global production, these biogenic sources include wetlands, rice agriculture, livestock, landfills, forests, oceans and termites, representing a flux of 167 Tg CH_4 y^{-1}. Non-biogenic CH_4 sources include emissions from fossil fuel mining and burning (natural gas, petroleum and coal) and account for 105 Tg CH_4 y^{-1}; biomass burning is responsible for 34 Tg CH_4 y^{-1}; waste treatment and geological sources (fossil CH_4 from natural gas seepage in sedimentary basins and geothermal/volcanic CH_4) around 64 Tg CH_4 y^{-1}. (Figure 1.1, Saunois et al., 2016, IPCC 2014).

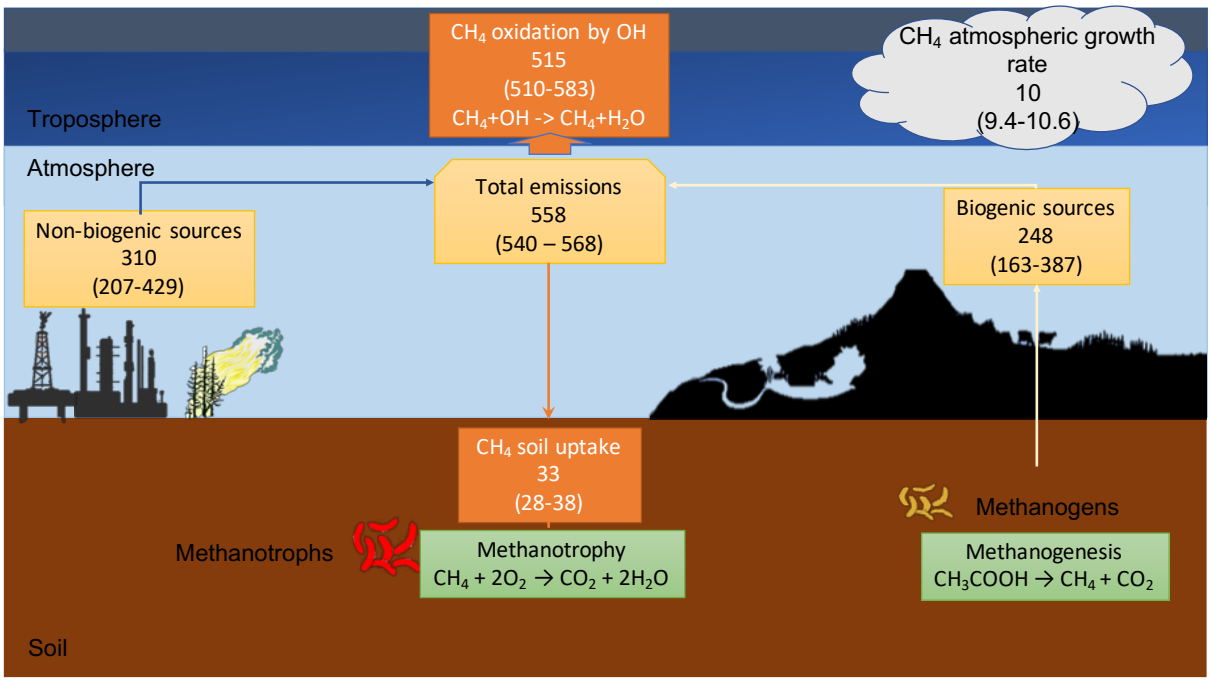

Figure 1.1 The global methane sources and sinks adapted from the Global Methane Budget 2002-2013 (Saunois et al., 2016). Sources indicated with yellow and sinks with orange. The units are teragrams of CH_4 per year (Tg CH_4 y^{-1}).

Biogenic CH_4 production is then driven by a process called methanogenesis, carried out by methanogens. Methanogenic microorganisms have been identified only from the domain Archaea and they are capable to produce CH_4 as a product of its anaerobic respiration. The two best described pathways involved either use acetic acid (CH_3COOH) and inorganic carbon dioxide (CO_2) as final electron acceptors, $CH_3COOH \rightarrow CH_4 + CO_2$ and $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ (Conrad, 1996).

The main sink of CH_4 is the troposphere via oxidation with OH (hydroxyl radicals), $CH_4+OH \rightarrow CH_3+H_2O$. The reaction sequence eventually leads to formaldehyde, then CO, and ultimately to CO_2 and H_2O (Crutzen et al., 1991). Almost 90% of the CH_4 is destroyed in troposphere, resulting in an atmospheric CH_4 lifetime of 9.6 years. In addition, about 1% of the CH_4 is lost in the stratosphere through the reaction of CH_4 with OH, Cl and O. Furthermore, it has also been observed that CH_4 is oxidized by reaction with chlorine radicals from sea salt in the marine boundary layer (1%) (Allan et al., 2007; Ciais et al., 2013). Finally, soils are the second largest, and the only biological sink, accounting for 9% of the total global CH_4 sink (Conrad, 2009). Soils also consume 90% of the CH_4 produced in the soil before it escapes to the atmosphere (Singh, 2010).

1.2 Methane consumption by soil

Methane (CH_4) consumption in the soil profile or methanotrophy is carried out by methanotrophs, soil bacteria that consume CH_4 as source of carbon and energy. Methanotrophs are unique using CH_4 as a source of energy, reacting CH_4 with oxygen and as a result producing carbon dioxide and water: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$.

There are 12 recognized genera of methanotrophs that are phylogenetically divided into type I (*Gamma proteobacteria*) and type II (*Alphaproteobacteria)*. Type I, also called "low affinity" methanotrophs requires a CH_4 concentration of >40 parts per million to be active (Hanson & Hanson, 1996). "Low-affinity" methane consumption is observed in all methane-producing soils (*e.g.* wetland, peat, landfill) (Bender & Conrad, 1992). "Low affinity" methanotrophs consume a large proportion of the CH_4 produced in soils before it escapes to the atmosphere (Reay et al., 2003). Type II methanotrophs are also known as "high affinity" methanotrophs. They are active at low CH_4 concentration of <12 parts per million and are found in soils that are characterized by diffusive methane supply from the atmosphere (*e.g.* forest soil). It has been estimated that they remove approximately 33 Tg of CH_4 from the atmosphere each year (IPCC, 2014).

The enzyme responsible for oxidizing CH_4 is the methane- monooxygenase, which occurs as both particulate and soluble forms. Well-characterized methanotrophic bacteria are obligate aerobes, they are found in all the upland soils in the world. In addition, several studies have reported methanotrophs in samples taken from muds, volcanos, swamps, rivers, rice paddies, the ocean, permafrost thaw ponds, streams, sewage sludge, floodplains and Artic mineral cryosol (Niemann et al., 2006; Miller et al., 2004; Sieburth et al., 1987; Schubert et al., 2006; Krause et al., 2010; Crevecoeur et al., 2015; Oshkin et al., 2014; Lau et al., 2015). There is evidence that these bacteria can be associated with aquatic plants in lake sediments and pond waters (Watanabe et al., 1997), as endosymbionts of mussels (Pond et al., 1998). CH_4 oxidation is observed in almost all environments on Earth, including, among others, the water column (Valentine et al., 2001), beneath ice shields (Wadham et al., 2013) or in hypersaline alkaline soda lakes (Kalyuzhnaya et al., 2008).

Despite the importance of CH_4 consumption in soils and the large increase of atmospheric CH_4 since preindustrial times (Kirschke et al., 2013), there are only few studies investigating the effect of increasing atmospheric CH_4 concentrations on soil methanotrophy. Laboratory studies indicate that, under real life conditions, soil consumption increases linearly with

increasing CH_4 concentrations (Bender & Conrad 1992; Nesbit & Breitenbeck,1992). Others have investigated the limits of the methanotrophic response under high CH_4 concentrations (up to 1000ppmv) and have observed that process rates continue to increase with no apparent limit (Henckel et al., 2000; Tuomivirta et al., 2009; Tate et al., 2012). These findings suggest that global CH_4 uptake will respond directly to the increase in atmospheric concentration.

Thus, our developing understanding of the mechanism of CH_4 oxidation at microbial scale and its response to different or changing environmental conditions not only enables to improve assessments of the significance of the global soil CH_4 sink and its spatial distribution, but also allows predictions of the soil's response to past, present and future climate change. In this respect, numerical, process-based global models are, in careful combination with observational and experimental data ideal tools to study global soil methanotrophy, as well as its response to global change (Chave et al., 2013).

1.3 Numerical modelling

Numerical models are efficient tools to evaluate the mechanistic understanding of physical and biological process that influence soil methanotrophy and to deal with the spatial and temporal variability. Additionally, they provide a platform of interdisciplinary knowledge and synthesis as they help identify key parameters and environmental controls, useful to direct future field and laboratory experiments. Finally, models can be used to integrate local and global data to generate estimates of soil uptake, a key step to predict the response of soil methanotrophy to past and future changes in climate and atmospheric conditions. The upscaling of microbial process, through the usage of numerical models, synthesizes information from a plethora of sources (*e.g.* remote sensing, direct measurements, flux towers, cruse data), fundamental to find global patterns and to identify gaps in our current understanding of global processes (Ebrahimi and Or, 2018). Thus, the modelling of global CH_4 consumption in the soils is an important developing topic in current earth system science (Ni & Groffman, 2018). In that sense two different approaches have been carried out to model the CH_4 consumption by soils: local and global models.

Several detailed biogeochemical models have been developed to quantify consumption of atmospheric CH_4 by soil at the local scale. Saggar et al. (2007) produced a modified version (NZ-DNDC) of Denitrification decomposition model (DNDC) (Li et al., 2000) to evaluate local impacts of changes in climate, soil properties, fertilizer management and grazing regimes on soil methanotrophy. Sabrekov et al. (2016) developed a process-based model of soil CH_4

uptake that also incorporates rhizosphere methanotrophy. Oh et al. (2016) developed eXplicit High-Affinity Methanotroph model (XHAM) that explicitly simulates high affinity methanotrophy and active microbial biomass dynamics (Table 1.1).

On the other hand, several process-based models have been developed to estimate global atmospheric CH_4 by soils, such as: Potter et al., (1996) based on Flick´s first law, which states that the diffusive flux under the assumption of a steady state, is going from the high concentration to the low concentration, with a magnitude that is proportional to the concentration gradient. This description of the diffusive flux has been used to estimate the diffusive atmospheric CH_4 into soil and the global uptake by soils. Ridgwell et al., (1999) based on Potter´s model, included the microbial oxidation process to estimate the global CH_4 consumption by soils. In the same family of models, Curry (2007) refined the mathematical representation of previous model, and the parameterization of the effect of water content into soil. Finally, one of the most recent global process-based models was developed by Zhuang et al. (2013), which is incorporated in the Terrestrial Ecosystem Model (TEM) and the refinements of microbial oxidation employs redox potential, ecosystem-specific inputs for Q_{10} and optimum soil moisture, given by TEM (table 1.1).

Table 1.1 Local and global- scale models to estimate atmospheric CH_4 consumption by soils.

Local scale			
Author/model	**Description**	**Input**	**Output**
Saggar et al., (2007) Denitrification decomposition model to New Zeeland NZ-DNDC	Process-based model to estimate CH_4 and N_2O fluxes and simultaneously models agricultural trace gas emissions, soil C sequestration, and crop yield	Mean daily climate parameters (temperature and precipitation). NO_3 concentration. Soil detailed characteristics (*e.g.* soil type, pH, organic carbon, ammonium and nitrite content), and land use agronomic practices information (*e.g.* tillage, fertilization, irrigation)	Farm-scale daily N_2O and CH_4 fluxes
Sabrekov et al., (2016)	Process-based model to estimate CH_4 consumption rate by	Climate parameters (*e.g.* temperature and soil moisture), soil properties (*e.g.* type, texture, pH, bulk	Atmospheric CH_4 uptake by methanotrophs in

	both rhizospheric and soil methanotrophs	density, organic and water content) Biological parameters (*e.g.* soil respiration, root biomass)	soil and in the rhizosphere.
Oh et al. (2016) eXplicit High-Affinity Methanotroph model (XHAM)	Numerical model to simulate the activity of high affinity methanotrophs	Climatic parameters (*e.g.* temperature and soil moisture) Biologic parameters (*e.g.* half saturation rate constant for CH_4 and acetate concentration, carbon use efficiency)	Activity of high affinity methanotrophs and microbial biomass, rates.
Global scale			
Potter et al., (1996)	Process-based model based on Flick´s first law	Climatic parameters (*e.g.* temperature and precipitation) Soil properties (*e.g.* porosity, water content and clay content)	Global atmospheric CH_4 diffusivity flux into soil
Ridgwell et al., (1999)	Improvement of Potter´s model by adding microbial oxidation process	Climatic parameters (*e.g.* temperature, evapotranspiration and precipitation) Soil properties (*e.g.* porosity, water content and clay content) Biological parameter (*e.g.* k_0 based microbial oxidation rate constant). Global agricultural fraction	Global atmospheric CH_4 oxidation rate by soils
Curry, (2007)	Improved of Ridgwell´s model by upgraded the mathematical representation of CH_4 diffusivity through the soil profile and re-parametrizing CH_4 diffusivity response to soil water content	Climatic parameters (*e.g.* temperature) Soil properties (*e.g.* porosity, water content and clay content) Biological parameter (*e.g.* k_0 based microbial oxidation rate constant) Wetlands extension Global agricultural fraction	Global atmospheric CH_4 oxidation rate by soils through the soil profile
Zhuang et al., (2013)	Process-based model to estimate global CH_4 uptake by soils, included in Terrestrial Ecosystem Model	Climatic parameters (*e.g.* temperature and optimum soil moisture for methanotrophy by ecosystem type) Soil properties (*e.g.* porosity, soil moisture, redox potential and clay content) Biological parameter (*e.g.* V_{max} and Q_{10} by ecosystem type) Nitrogen deposition	Hourly methanotrophy rates within each 1 cm layer of the soil profile

Despite of the advances of the CH_4 uptake modelling, existing local and global models that simulate atmospheric CH_4 uptake by soils reveal several limitations that compromise their ability to simulate the global mean uptake and its variation through time and space. For instance, complex, local models require high resolution local data sets, thus rendering their application on the global scale and for future and past periods impossible, due to the limited availability of comprehensive input data sets necessary to drive the models (*e.g.*, global rhizosphere depth, specific soil management, specific metabolic data, enzyme concentrations). On the other hand, most of the current global process-based models were developed at a time of limited data availability both with respect to global observational forcing data (*e.g.* nitrogen inputs) and direct field and laboratory measurements suitable for model validation. As a consequence, none of the existing global models has been thoroughly validated on the basis of field data. In addition, their parametrization and structure need to be revisited in the light of our growing mechanistic understanding of soil methanotrophy and its drivers.

1.4 Drivers of soil methanotrophy

Interestingly, all of the existing global process-based models consider two fundamental process to model methanotrophy: the diffusion rate of CH_4 into the soil (substrate availability) and the microbial capacity to oxidize it. Both processes are controlled by a number of environmental factors (Figure 1.2). Thus, by focusing on these two processes and their controls we can advance the modelling and understanding of the global CH_4 uptake.

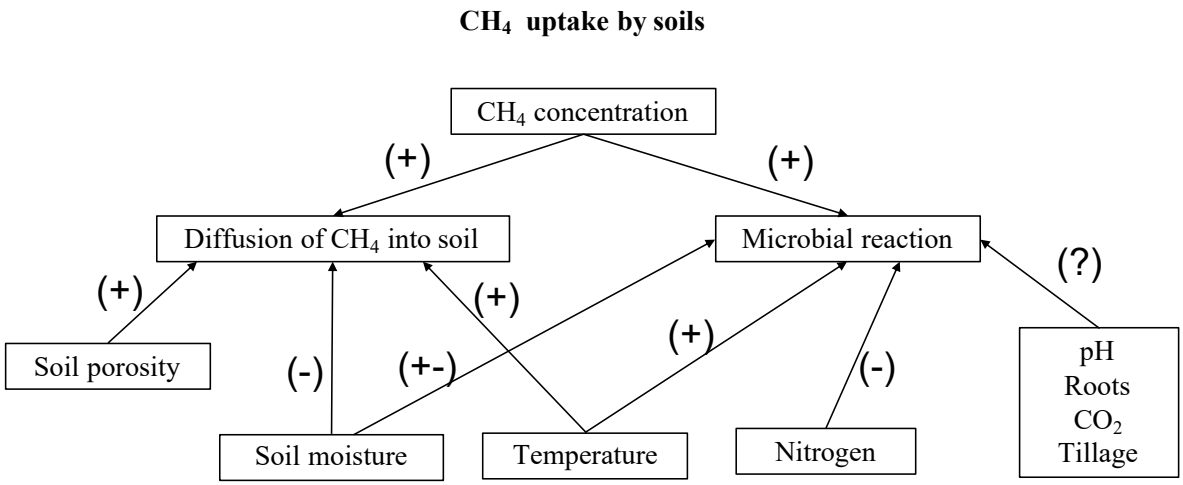

Figure 1.2 Main driving factors of CH_4 uptake by soils. Diagram of the effect of every factor in the CH_4 consumption by soils. Every arrow represents an equation and the symbols (+) and (-) show the general effect of the relationship between the components.

1.4.1 The diffusion rate of CH_4 into the soil

CH_4 transport from atmosphere into the soil is the main source of substrate for the methanotrophs. In general, the capacity of methanotrophs to consume CH_4 exceeds the potential of CH_4 to diffuse or penetrate in the soil profile (Striegl, 1992), thus diffusion driven partially by atmospheric CH_4 concentration is usually the main limiting factor of the process. Some direct measurements of CH_4 penetration in soil profile have been made under laboratory conditions showing that the maximum oxidation rate of CH_4 occurs around the first 0-40 cm (Schnell & King 1996; Hütsch,1998; Visvanathan et al., 2002; Stackhouse et al., 2015) however this depends of CH_4 concentration, soil type, temperature and soil moisture.

Soils are a porous matrix containing gases and water that is exchanged with the atmosphere and soil type thus exerts a strong control on gases diffusion and on CH_4 flux. Dutaur & Verchot (2007) proved, that soil texture is the main factor controlling CH_4 fluxes and sandy and loam soils consumed more CH_4 than clay soils. The main physical limitation for the gas diffusion into soil is the water content inside the porous media and solid particles causing water blockages for gas transport (Figure 1.3). Thus, the diffusion of CH_4 into soil is controlled by soil-solid and soil-water dynamics (Moldrup et al., 2013).

Some models have simulated the dynamic of CH_4 diffusion into soil. One of the first local models to resolve the dynamics of water content for different depth intervals was Striegl, (1992). The first model to employ atmospheric CH_4 diffusion into soils at global scale was developed by Potter et al. (1996), which was based on Fick´s first law, parametrizing the CH_4 diffusivity in aggregated media, together with a soil water balance. Other authors continued improving the model representation of this process by implicitly accounting for the effect of microbial CH_4 oxidation in the diffusion equation (Ridgwell et al., 1999). They used the same CH_4 diffusivity parametrization than Potter et al. (1996), but solved the transport equation analytically, thus only estimate the uptake for a layer of soil. Later, Curry (2007) and Zhuang et al. (2013) proposed different process-based models that are based on a vertically resolved diffusion equation that is solved by assuming an infinite penetration of CH_4 into the soil or a fixed concentration (based on biological parameters) at a maximum depth of 100 cm. As a consequence, no model currently allows for a dynamic calculation of diffusive CH_4 penetration into the soil without making explicit assumptions about the lower model boundary.

1.4.2 Microbial oxidation

1.4.2.1 Microbial oxidation constants k_0 y V_{max}

Microbial CH_4 oxidation is an enzymatically mediated process. As a result, it is controlled by microbial biomass dynamics, community structure, substrate (CH_4) concentration and a complex array of environmental factors, including temperature, land use, moisture, pH and soil type (Ho et al., 2013), followed by pH, CO_2, root dynamic, and soil management (*e.g.* tillage) (Aronson et al., 2013). CH_4 oxidation rate constants can be defined either on the basis of theoretical considerations or through site-specific field and laboratory observations. These rates have been modelled by two approaches: the V_{max} (maximum oxidation rate) and k_0 (base oxidation rate) parameters.

Models based on V_{max} measure the maximum reaction rate at a saturation point of substrate. Being a kinetic reaction of zero-order, the enzymatic activity is directly proportional to the enzyme concentration and independent of the substrate concentration. Maximum rates have only been measured under laboratory conditions for methanotrophy and fall into the range 270–3690 nmol CH_4 $h^{-1}g^{-1}$dw (Bender & Conrad, 1992; Smith et al., 1997; Park et al., 2005; Vishwakarma & Dubey 2010; Kravchenko, 2002). All these studies assume that V_{max} is dependent of environmental factors such as: temperature, soil moisture, pH, nitrogen concentration and the bacterial structure and phylogeny.

Microbial oxidation is also often described by a first-order kinetic rate law with a rate constant k_0, thus assuming that the enzyme activity is directly proportional to the substrate concentration. First order rate laws generally apply to the base oxidation rate constant, k_0, for an uncultivated moist soil at 0º C. This has usually been determined on theoretical basis from long-term and specific-site field measurements, even though k_0 also can be determined directly for field or laboratory experiments. Applied k_0 values for soil methane uptake fall within the range $1.6x10^{-5}$ and $8.7x10^{-4}$ s^{-1} (Ridgwell et al., 1999; Curry, 2007; Murguia-Flores et al., 2018).

Both approaches have advantages and limitations. The determination of V_{max} requires experimental conditions of substrate saturation, which are difficult to determine under field conditions. In addition, reaching CH_4 saturation points under *in-situ* is practically impossible, limiting the number of available measurements. One example of its application is the global process-based model of Zhuang et al., (2013). They used modelled V_{max} for different ecosystems at the global scale. However, the parametrization was not compared with observed in-situ rates, due to their limited availability. On the other hand, k_0 is a parameter that can be determinate directly from long-term CH_4 uptake flux measurements, across specific ecosystem soils. However, due to the specificity of the measurement (0º C and 20% moisture) calculations

can differ greatly. More importantly, in order to obtain this parameter, long-term measurements or their direct determination for specific sites are needed. However, such measurements are sparse globally. Current models that use this parameter, usually employ a single value for the entire planet (*e.g*. Curry et al. 2007) despite evidence for variations across ecosystems (Bender & Conrad, 1992).

1.4.2.2 Temperature

The effect of temperature on gas diffusion is always positive, as the process is governed by the ideal gas law. Thus, at a higher temperature there are more molecules per volume of air, leading to faster diffusion rates (Moldrup, 2001).

The microbial CH_4 oxidation rate is also affected by temperature, following a Q_{10} response. This is a positive relationship until an optimum, estimated between 25-35º C in forest soils (Bender & Conrad, 1992; Dunfield et al., 1993; Castro et al., 1995; Mohanty et al., 2007) and between 30-36ºC in landfill cover soils (Whang et al., 2011) is reached. At higher temperatures, a decrease in the methanotrophy is observed and activity generally ceases above 45º C (Bender & Conrad, 1992; Dunfield et al., 1993; Castro et al., 1995; Mohanty et al., 2007). The latter is governed by the enzymatic nature of the process. If ambient temperature rises above the optimum, the function of the enzyme decreases until its denaturalization. Similarly, when temperature is too low (below 0º C) an attenuation of enzymatic activity and a limitation of liquid water can be observed. However, there is evidence of methanotrophic activity in Siberian permafrost and subglacial environments until -10ºC (Khmelenina et al., 2002). It is also noteworthy that some methanotrophs communities in Siberian permafrost and Artic cryosols seem to be adapted to low temperature conditions and the uptake reaches an optimum between 5-5.6 ºC (Khmelenina et al., 2002; Lau et al., 2015). Temperature is a limiting factor of CH_4 uptake in the coldest regions and in permafrost (Dunfield et al., 1993; Lau et al., 2015) at a global scale, this factor reveals a latitudinal pattern with lower uptake rates over the high latitudes due to the spatial extension of frozen soil and a seasonal pattern due to temperature optimum for methanotrophs. The previous implies that at the face of climate change methanotrophy will respond differently to the reduction of frozen soil extension and the increase in growing season.

Additionally, temperature has a strong effect over the methanotrophs population, and has proved to be an important factor regulating the community composition. Soil incubation experiments have shown that high-affinity methanotrophs are about 2–3 times as sensitive to

temperature as low-affinity methanotrophs (Börjesson et al., 2004; Mohanty et al., 2007; Christiansen et al., 2015; He et al., 2012; Jørgensen et al., 2015; Lau et al., 2015). These shifts in methanotrophs composition affect the microbial oxidation rate at the same time.

The most common way to model the effect of temperature on the methanotrophic bacteria is by employing a Q_{10} factor. The term Q_{10} is a commonly used measurement of the rate of change in a biological system as a consequence of increasing the temperature by 10°C. In most biological systems on ranges between 1.5-2.5 and has been shown to be a key measurement of biological performance (Hegarty, 1973). The Q_{10} value reported for methanotrophy across a wide range of ecosystems lies between 1.1 and 3.0 (King and Adamsen, 1992; Dunfield et al., 1993; Lau et al., 2015).

Temperature in global process-based models affects both CH_4 gas diffusion in soil and microbial oxidation rate (Ridgwell et al., 1999; Curry 2007; Zhuang et al., 2013). First, increased temperature accelerates diffusion due to the increase of kinetic energy and velocity of the gas particles. Secondly, temperature can exert both a negative and positive effect on base oxidation rate k_0 (Ridgwell et al., 1999; Curry 2007; Murguia-Flores et al., 2018), or V_{max} (Zhuang et al., 2004).

1.4.2.3 Soil moisture

Soil moisture is the main limitation for the diffusion of CH_4 into soil. The pore-space free of water is the media to diffuse CH_4. Thus, wet conditions limit microbial activities by restricting CH_4 and O_2 diffusion, and dry conditions limit microbial activity due to physiological water stress. The maximum CH_4 oxidation rate has been calculated for different soil moisture contents (%) in a range of ecosystems under both field and laboratory conditions. The optimum has consistently been estimated between 15-25% for soils of multiple ecosystems. In addition, the same studies reported no methanotrophy at <5% or >50% of soil moisture (Boeckx & Van Cleemput, 1995; Bowden et al., 1998; van den Pol-van Dasselaar, 1998; Visvanathan et al., 1999; Nesbit & Breitenbeck, 1992; Whalen et al., 1990; Gulledge & Schimelb, 1998; Adamsen & King 1993).

At the local scale, soil moisture is an important driving factor of methanotrophy, which is determined by specific conditions, such as precipitation and relieve. Soil moisture is influenced directly by precipitation, resulting in a distinct seasonality of CH_4 uptake in ecosystems driven by rain, such as the tropical dry forest. Singh et al., (1997) found higher amounts of CH_4 consumption during the dry season than during the rainy season. On the other

hand, soil moisture is determined by the exact location of the soil in the landscape and its position on the slope. Thus, higher uptake has been reported on south facing slopes on forest and tundra of the Northern Hemisphere (Whalen et al., 1996; West et al., 1999) due to their higher evapotranspiration rates making them drier and more suitable for CH_4 oxidation by methanotrophs.

At the global scale, soil moisture drives a regional and seasonal pattern with high CH_4 consumption over arid regions and low consumption over wet regions. Therefore, shrublands and savanna represent the strongest sinks for CH_4 and the dry season generally reveal higher uptake rates that wet seasons (Potter et al., 1996; Zhuang et al., 2013).

Due to its importance, soil moisture is a factor that has always been considered in all models of global soil CH_4 uptake. It is usually assumed that it controls both processes that determine CH_4 uptake: diffusion and microbial oxidation rate. For the first, water content in soil is estimated based on precipitation and evapotranspiration (as there were not soil moisture data), this parameter together with soil type (soil texture and porosity) determines the available pore space for gas exchange (Potter et al., 1996; Ridgwell et al., 2009; Curry 2007). For the second process, in existing global models soil moisture is assumed to limit microbial oxidation rates only under dry conditions (Ridgwell et al., 1999; Curry 2007), while the negative effect of high soil moisture has only been recently included by Zhuang et al, (2013). The authors used multiple values of optimum soil moisture depending of ecosystem type (simulated). However, to my best knowledge, there is currently no global model that accounts dynamically for the negative effect of high soil moisture on microbial oxidation rates.

1.4.2.4 Nitrogen

Observations indicate that nitrogen (N) exerts a negative effect on CH_4 uptake by the soil (Aronson & Helliker, 2010; Butterbach-Bahl & Papen, 2002; Steinkamp et al., 2001). This inhibition has been shown at three different spatial scales: at the cellular level, the microbial community level and the whole ecosystem.

At the cellular scale, N inhibits the CH_4 oxidation via three mechanisms. First, methanotrophs and ammonia oxidizers are capable of shifting substrates. Facultative methanotrophs can use N compounds as a source of energy, as ammonia oxidizer bacteria do and vice versa (Hanson and Hanson, 1996). This leads to a reduction in the CH_4 oxidation with N additions (Wang et la., 2016; Zheng et al. 2014). Second, the intermediates and end products of methanotrophic ammonia oxidation, i.e. hydroxylamine and nitrite, can be toxic to

methanotrophic bacteria and also lead to inhibition of methane consumption (Mohammadi et al., 2017). Finally, the excess of ammonia fertilizers salts induces osmotic stress to methanotrophs and reduce the CH_4 consumption (Bodelier et al., 2004).

At the community level, there is only one known mechanism that alters the CH_4 consumption rates, a shift in bacterial community structure. In particular, N additions can alter the population ratios between ammonium- tolerant and ammonium-intolerant methane-oxidizing species. Recent studies found that the methanotrophic community was significantly affected by the different fertilizer treatments across different ecosystems. For example, on rice field soils (Sherestha et al., 2010) and forest soils (Jang et al., 2011), N addition selectively inhibited Type I methanotrophic bacteria and that lead to a decrease in the uptake. However, the opposite effect - N stimulation of CH_4 uptake- also has been observed on rice cultivated soils, forest and landfills (Cai et al., 2000; Rigler et al., 1999; De Visscher et al., 2001). The mechanism that explains this pattern supposes an opposite effect, which is a stimulation of nitrifying bacteria to consume CH_4 by the increased inputs of N due to an improvement in living conditions. The directionality of the response is dependent on the original community structure and dynamic, previous soil N concentrations and the spatial arrangement of methanotrophs community in the soil profile (Bodelier et al., 2004). Thus, under particularly low N conditions, the addition of the element can lead to an increase in the uptake; however, the opposite effect has been reported for almost every ecosystem.

The effect of N on CH_4 uptake at ecosystem level has been evaluated both directly, adding N (Steudler et al.,1989; Zhang et al., 2008; Wilson et al., 1995) and indirectly, evaluating the effect of land use change between natural and agricultural soils (Dobbie et al 1996; Tate et al., 2007; Singh et al., 1997; Luo et al., 2013). In both direct and indirect fields measurements, N was found to have a negative effect on the uptake. For example, in grasslands the addition of fertilizers of N lead to a long-term decrease of 40% in CH_4 uptake by the soils (Steudler et al., 1989). Additionally, the mean reduction in uptake rates resulting from conversion to agriculture was 60% compared with forest/woodland and agricultural land, in Scotland, Denmark and Poland (Dobbie et al., 1996). At this level, the N effect also depends of the previous state of the soil before the N application. For example, N-low additions can enhance CH_4 uptake in perturbed areas (Xu, et al., 2014; Zheng et al., 2016) and also present a seasonal effect due to soil moisture and temperature (Yue et al., 2016). Thus, the general effect of N addition on the soil CH_4 uptake is usually negative at ecosystem level; however under limited conditions of high N deficiency (*e.g.* altered sites), N addition may lead to a small increment in the process.

Several models that evaluate CH_4 uptake by soils at specific-site scale take into account the dynamic of N in the soil (denitrification and nitrification) and the active microbial biomass dynamics. For example, both process-based models used to estimate CH_4 uptake by soils: the denitrification-decomposition to New Zeeland model (NZ-DNDC) and the eXplicit High-Affinity Methanotroph model (XHAM). However, the specific driving data that those models use to evaluate the N and methanotroph dynamics compromises their applicability at a global scale due to the lack of available data. Other, simpler global process-based models (Ridgwell et al., 1999; Curry, 2007), included the negative effect of N addition on the uptake using the agricultural area (%) as a proxy of regions with N inputs through a negative linear relationship. They assume a reduction in the uptake by a factor of 75% when land is fully converted with croplands. More recently, Zhuang et al., (2013), used a more sophisticated approach for the inhibition of CH_4 uptake by N. First, they modelled the distribution N in the soil profile and then calculated the inhibition factor (based on Snell & King, 1994), using global N deposition as forcing data. This approximation yielded more realistic inhibition values than the previous global models, however, this approach is limited by recent findings (from field and lab) that evaluate the link in both cycles and by the lack of N additions via inorganic fertilization applications.

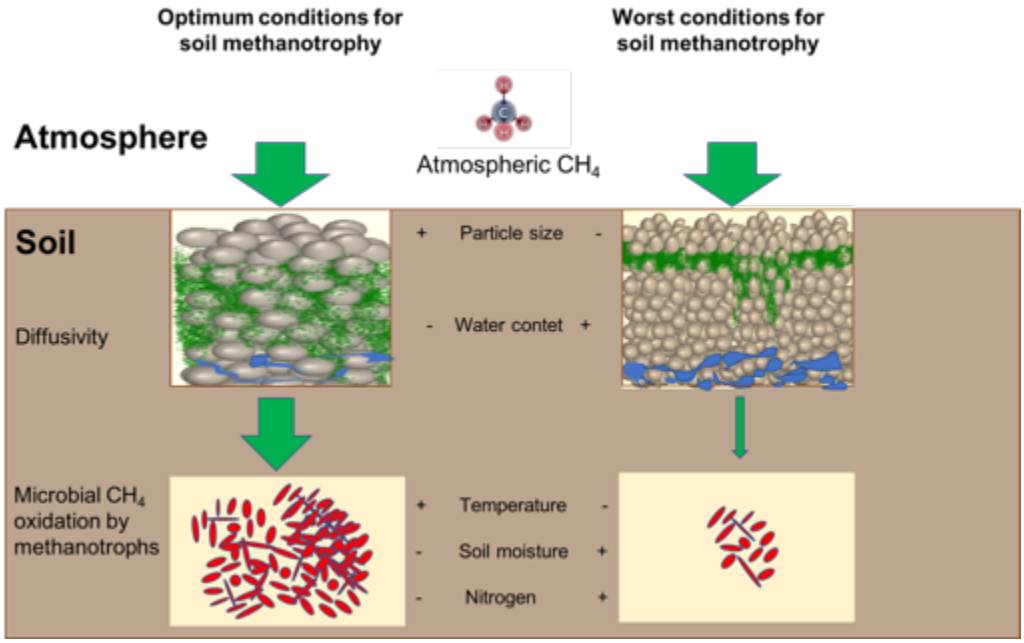

Figure 1.3 Schematic representation of both, optimal and non-optimal conditions for soil methanotrophy. Soil uptake of CH_4 is determined by two processes: diffusion of CH_4 into the soil, controlled by soil type and water content, and the microbial oxidation, controlled by temperature, soil moisture and nitrogen concentration. Green arrows represent the atmospheric CH_4 flux and the blue spots the soil water content. Symbols + and – represents when the

conditions are optimal or not optimal for CH_4 uptake. The thickness of arrows represents the magnitude of the CH_4 flux.

1.4.2.5 Other driving factors

There are other factors that affect CH_4 oxidation by soil methanotrophs to a lesser extent, such as: pH, rhyzosphere activity, CO_2 and tillage. Methanotrophy is highly sensible to pH and there is evidence that CH_4 uptake rate decreases with pH and high CH_4 oxidation rates have been registered in calcareous soils with neutral pH (Hütsch et al. 1994; Hütsch 1998; Mc Namara et al., 2008). Some authors report an optimum pH for methanotrophy around 5.8 (Amaral et al., 1998).

Secondly, there are studies that suggest a positive effect of rhizosphere activity on CH_4 uptake. For example, Subke et al. (2018) found a positive effect of ectomycorrhizal mycelium and CH_4 uptake; Feng et al., (2017) proposed a theoretical model to include the root architecture showing how this can influence the methanotrophs abundance and therefore affect the CH_4 oxidation rates. Additionally, other studies have separated soil CH_4 uptake from methanotrophy in the rhizosphere to improve estimates of total CH_4 uptake (*e.g.*, Sabrekov et al., 2016).

Several studies have investigated the effect of CO_2 concentration on the CH_4 uptake showing a reduction (~30%) in the uptake flux with an increase in CO_2 flux (Phillips et al., 2001). The mechanism of this effect is still unknown, but one possibility is the increase in soil moisture due to an enhanced vegetation growth via CO_2 fertilization (McLain et al., 2002).

Finally, tillage enhances the aeration and increases soil porosity. Tillage is a common practice in agricultural land. However, its effect on methanotrophy is not well defined. Several studies have found a general positive effect of this practice on CH_4 consumption in agricultural soils due to the increase in bulk density and porosity that promote CH_4 diffusion (Dam et al., 2005; Lampurlanés & Martinez, 2001; Bauer & Blak 1981; Unger & Jones 1998; Osunbitan et al., 2005 and Grant & Landford, 1993). However, it should be noted that it is difficult to separate the tillage and fertilization effects.

All those factors are not included in most of the existing global process-based models. Even though they can be modelled and parameterized, most of these factors are difficult to constrain on a global scale either because of the lack of data (*e.g.* root dynamic) or because the mechanism behind them is not well understood (*e.g.* CO_2). Nevertheless, some of these factors such as tillage and pH can be constrained (at least to a first degree). They be included in global

models to evaluate their significance on soil uptake on a global scale as well as the to assess the response of the global CH_4 soil sink to land-use changes.

1.5 The response of the global soil CH_4 sink to changes in past and the future climate.

The previous sections provide a detailed overview of how CH_4 uptake by soils can vary with changes in the environmental factors that drive the process. All these environmental factors and thus the two process that control soil CH_4 uptake vary, have varied and will vary on both spatial, and temporal scales. Yet, studies that investigate how methanotrophy has varied and will vary as a result of changes in its drivers are currently lacking. For example, in terms of the past record, atmospheric CH_4 concentration, temperature and soil moisture have greatly varied. Over the last million years, the concentration of CH_4 in the atmosphere has fluctuated from 300 to 900 ppbv (Petit et al., 1999), showing a direct relationship with temperature, due to natural changes in the Earth's orbit known as Milankovitch cycles. Due those changes it is possible that uptake changed accordingly, but we ignore the magnitude.

Since the last glaciation, the CH_4 concentration in the atmosphere rose from 375 ppbv during the last glaciation maximum (LGM) 21,000 years ago to 680 ppbv at the beginning of the preindustrial era (Figure 1.4). The reduction of atmospheric CH_4 during LGM was explained by the decrease in the CH_4 lifetime arising in part from reduced the volatile organic compounds (VOC) emissions (Valdes et al., 2005; Kaplan et al., 2014) and the reduction in number and area of wetlands, the main biogenic source of CH_4. The climatic conditions during this period were extraordinary with vast ice sheets covering much of North America, northern Europe, and Asia. The climate was affected, and the average global temperature dropped to 6º C causing drought, desertification, and a dramatic drop in sea levels (Levine et al., 2011). The subsequent warming led a posterior increase in CH_4 due to the increase in wetlands. As a result, the CH_4 uptake by soils varied with atmospheric CH_4 concentration. Yet, there are only a few estimates of the size of the soil CH_4 sink for the geological past. For example, Hopcroft et al., (2017) estimated a global uptake of 11 Tg CH_4 y^{-1} during the LGM, while other authors assumed no change in soil uptake since LGM and through Holocene, estimating a constant 10 Tg CH_4 y^{-1} (Chappellaz et al., 1993). Thus, there is a lack of data of the changes in the uptake through this time based on the climatic and atmospheric CH_4 changes and an analysis of its contribution to the global budget.

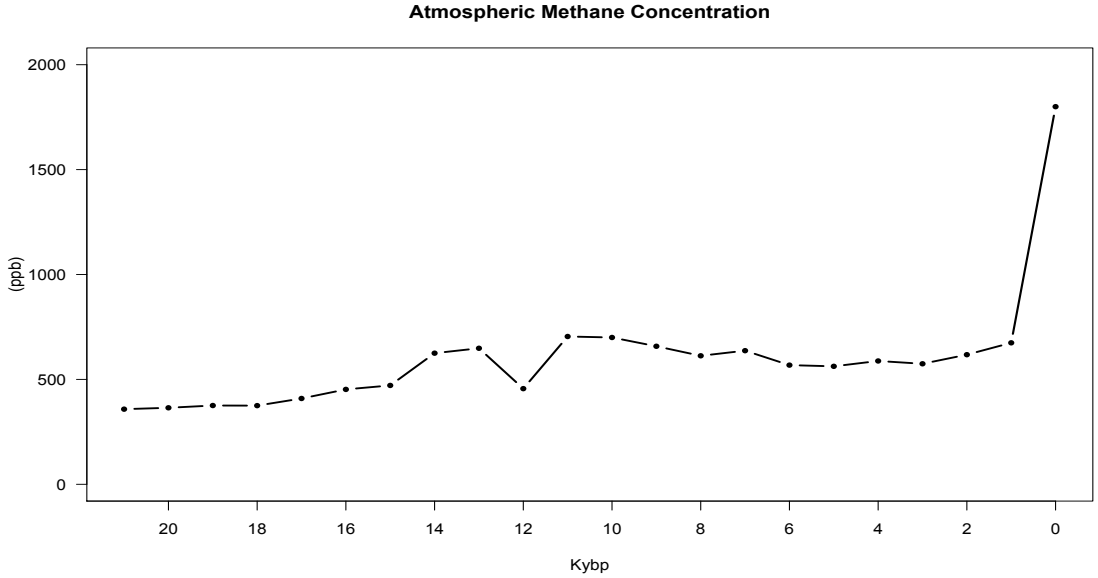

Figure 1.4 Evolution of atmospheric CH_4 concentration (ppb). By slices of 1000 of years, from LGM (20 Kybp) to 2016 (0 Kybp)

Furthermore, since the industrial revolution there has been a significant increase in global atmospheric CH_4, increasing from 680 to current 1800 ppb, driven directly by the human emissions (Figure 1.4, Kirschke et al., 2013). As a result, there has been an increase in the soil sink for the last century. Estimates of the global uptake based on extrapolated observations range from 28-33 Tg y^{-1} (Dörr et al., 1993; Smith et al., 2000; Dutaur & Verchot, 2007), atmospheric inversions models predicted 30 ± 15 Tg y^{-1} (Hein et al., 1997), while global model estimates indicate an uptake of 20-38 Tg y^{-1} (Potter et al, 1996; Ridgwell et al., 1999, Curry 2007; Spahni et al., 2011). For the full century, Zhuang et al., (2013) estimated a global uptake between 32-36 Tg y^{-1} with an acceleration of 0.03–0.20 Tg CH_4 y^{-2}. It is thus clear that the CH_4 uptake by soils has changed during the last century, but the attribution of this changes is not well understood as well as the causes and the mechanism behind it.

For the future, global warming will drive a change in environmental conditions. The fifth Assessment Report published in 2014 of the IPCC proposed four Representative Concentrations Pathways (RCPs) updating the emission reports in emission scenarios (SRES) published in 2000. The RCPs describe four possible future climate scenarios based on the amounts of greenhouses emitted in the years to come. The four RCPs are named after their radiative forcing values in 2100, relative to preindustrial values (+2.6, +4.5, +6.0, +8.5 Wm^{-2}). Based on the previous climatic conditions predicted by the SRES (IPCC, 2000), Curry (2009) and Zhuang et al., (2013) estimated an increase in the uptake compared with present day, between 23 and 280%, respectively. Their estimations were based on the extremist low and

high scenarios. The increase in uptake was explained by the increase in atmospheric CH_4 concentration. However, there is currently no assessment of the soil CH_4 uptake and its response to climate change for future years using the current RCPs.

Finally, methanotrophy in the soils has been relegated as a small contributor to the global CH_4 sink; however, the proportion of atmospheric CH_4 that soils consume every year plays a fundamental role in deaccelerating the rise of atmospheric CH_4 concentration. the percentage of atmospheric CH_4 consumed by the soils every year could be a potential unexplored indicator of the how climate alters methanotrophy. Theoretically, as the only biological sink of CH_4 this can be directly altered not only by the variation in atmospheric CH_4 but by the variation of climate, thus, the process should consume a constant fraction of the atmosphere and during extreme climate transitions, the ratio should be modified.

In summary, CH_4 uptake by soils, its role in the CH_4 cycle and contribution to the global CH_4 budget has changed and will change with climate change and variations in the atmospheric CH_4 concentration. Yet, the magnitude of this change, as well as the change in the relative significance of each factor that controls CH_4 uptake in response to past and future climate remains unconstrained and its role in the global CH_4 budget is thus limited.

Objectives

The main objective of my PhD thesis is therefore: To improve our understanding of the global CH_4 consumption by soils across different temporal and spatial scales. In order to achieve this, I developed four particular objectives, which extend as the chapters of my thesis.

Objective 1: To develop and test a novel process-based model to estimate the global CH_4 uptake by soils that is informed by our advancing mechanistic understanding of soil CH_4 uptake.

In the second chapter of my thesis a novel process-based model for CH_4 uptake by soils was developed, based on previous models from Potter et al., (1996); Ridgwell et al., (1999) and Curry (2007). This was motivated by the need to review model construction in the light of new available observations and measurements, as well as the availability of improved forcing data, such as, global nitrogen inputs from fertilizers or soil moisture from satellite observations. The mathematical solution of the transport-rate equations was improved to include: 1) a dynamic CH_4 penetration that is explicitly calculated based on process rates rather than imposed and 2) allowing for the inclusion of a flux coming from below the simulated soil profile. In addition, the parameterization of the temperature and soil moisture effect on the microbial oxidation rate were revised based on published observational data and correcting the negative effect at high soil moisture. The inclusion of different oxidation rate constants, $k_{0,}$ for different ecosystems was possible due to the recent emergence of long-term direct flux measurements from three different ecosystems. For the first time in a global model, the nitrogen inhibition effect through fertilization and deposition was included. The model is fully described and the validation, limitations, potential applications and avenues for future research are also discussed.

Objective 2: To evaluate the spatial and temporal dynamics of global CH_4 uptake by soils.

The spatial and temporal of the components of the global CH_4 cycle remained uncertain. This is especially true for the CH_4 sinks. Soil methanotrophy, the only biological sink, at global scale, responds to the variability of environmental conditions across ecosystems. Additionally, ecosystem exhibit distinctive climatic conditions depending on latitude through a year leading to seasonality and interannual variability in the uptake fluxes. The understanding of temporal

and spatial changes in this sink are important factors required to determinate the effects of changes in future climate. Therefore, Chapter three explores the spatial and temporal dynamics of global atmospheric CH_4 uptake by soils, as well as the uptake across different ecosystem types and their seasonal dynamics.

Objective 3: To evaluate the contribution of CH_4 uptake by soils to the global budget. To evaluate its feedback on climate change (radiative forcing) and to attribute the changes in the past century (1990-2015) and future scenarios (2016-2100) to its drivers.

Methanotrophy has been neglected as a minor part of the CH_4 cycle due to its relatively small contribution (9-10%) to the overall sink. However, its contribution has varied through time and it is possible that it will play a more important role in the future. In the fourth chapter of this thesis, the model developed in Chapter 2 is applied to evaluate the present and future role of methanotrophy in the global CH_4 budget. The main factors that control the change in the uptake were quantified for the last century (1900-2015) and future scenarios, using the recent RCPs scenarios (2016-2100). The mechanism behind the change in the uptake were analyzed for the future scenarios. For example, the increase in the number of days with active methanotrophy, changes in soil moisture, changes in cropland area were considered. Finally, the evaluation of CH_4 soil uptake on climate change was measured through the usage of radiative forcing, determining the mitigation potential of the process in the future.

Objective 4: To evaluate the changes in CH_4 uptake by soils since the last glaciation maximum.

There are only a few estimations of the CH_4 uptake by soils for the geological past and thus little insights on its variation through time. In chapter five, the newly developed model is applied to simulate the CH_4 uptake from the last glacial maximum to the present. An estimation for the consumption of CH_4 by the soils was calculated for this using state-of-the-art climate model output as driving data. The driving factors of change were analyzed to obtain a general perspective of their contribution to the variation in the CH_4 uptake by soils during the last 21,000 years.

CHAPTER 2

Soil Methanotrophy Model (MeMo v1.0): a process-based model to quantify global uptake of atmospheric methane by soil

Contributions and acknowledgements

This chapter is adapted from a research article published in *Geoscientific Model Development* (Murguia-Flores et al., 2018). All co-authors (S. Arndt, A. L. Ganesan, G. Murray-Tortarolo & and E. R.C. Hornibrook) provided assistance with editing and advised on aspects of this work. Three anonymous referees gave insightful comments on previous versions of the published manuscript. All work presented in this chapter is my own.

Murguia-Flores, F., Arndt, S., Ganesan, A. L., Murray-Tortarolo, G., & Hornibrook, E. R. C. (2018). Soil Methanotrophy Model (MeMo v1. 0): a process-based model to quantify global uptake of atmospheric methane by soil. *Geoscientific Model Development*, *11*(6), 2009-2032.

2.1 Introduction

Numerical models provide an efficient means to deal with the spatial and temporal heterogeneity and to evaluate mechanistic understanding of physical and biological processes that influence soil methanotrophy. Ultimately, models enable derivation of regional and global estimates of soil uptake of atmospheric CH_4 and provide the ability to predict the response of soil methanotrophy to past and future global change. In addition, they provide a platform of interdisciplinary knowledge synthesis, help identify the most important parameters and environmental controls, and can thus inform future field and laboratory research. Existing models to estimate atmospheric CH_4 uptake by soils globally need to be revisited and reevaluated periodically in the light of novels findings, as such models for the soil uptake of CH_4 are behind the current available global data and lack the inclusion of some fundamental processes (e.g. nitrogen inputs from fertilizers).

Previous global models included Potter et al. (1996) (hereafter referred to as 'P96' model), which estimates terrestrial uptake of CH_4 by calculating diffusive flux of atmospheric CH_4 into soil using a modified version of Fick´s first law. Ridgwell et al. (1999) (hereafter

referred to as 'R99' model) improved the P96 model by explicitly accounting for microbial CH_4 oxidation in soil. The R99 model quantifies CH_4 oxidation rates as a function of soil temperature, moisture and N content. The latter parameter was estimated using agricultural land area as a proxy for fertilizer application. Solution of the resulting one-dimensional diffusion-reaction equation was approximated semi-numerically assuming steady state conditions. Curry (2007) (hereafter referred to as 'C07' model) employed a steady state analytical solution of the one-dimensional diffusion-reaction equation and introduced a scalar modifier to account for the regulation of CH_4 oxidation rates by soil moisture and the impact of temperature below 0°C. The C07 model continued to use the R99 agricultural land area approximation to evaluate the effect of N loading on CH_4 uptake. The C07 model has been employed as a reference model for the Global Carbon Project (Saunois et al., 2016) and has been used to estimate global CH_4 uptake in dynamic global vegetation models, such as the Lund-Potsdam-Jena model (LPJ-WHy-Me; Wania et al., 2010; Spahni et al., 2011).

The model of Zhuang et al. (2013) (hereafter referred to as model 'Z13') employs the same steady state reaction-diffusion equation for CH_4 as previous models; however, Z13 solves the steady state reaction-diffusion equation for CH_4 numerically using multiple soil layers. Additionally, parameterization of microbial activity in model Z13 is based upon redox potential, ecosystem-specific inputs for Q_{10} and optimum soil moisture, and maximum rates of CH_4 consumption instead of a base rate for CH_4 oxidation. Consequently, model Z13 operates within the Terrestrial Ecosystem Model (TEM) that provides the necessary driving data because global data sets for many of these parameters are not available. If external data were available, model Z13 presumably could be operated independently of the TEM in a manner similar to models P96, R99 and C07. However, such a stand-alone application (*i.e.*, decoupled from TEM) would require a new implementation or presumably significant modifications to the code.

This chapter focuses on refining the R99 and C07 models because availability of new observational and experimental data presents an opportunity to re-evaluate global simulations of soil methanotrophy based upon an enhanced version of these models. For example, new global datasets quantifying N deposition and N input via fertilizers now enable better representation of this inhibitory effect on soil uptake of atmospheric CH_4 (Lamarque et al., 2013). In addition, a new global inventory of CH_4 uptake rates in soil (Duataur & Verchot, 2007) provides a means to better compare and valid model simulations.

Therefore, in this chapter a novel process-based model to quantity the global sink for atmospheric CH_4 by soil (hereafter referred to as 'MeMo': soil **Me**thanotrophy **Mo**del) is

presented. MeMo is based on a general analytical solution of the one-dimensional diffusion-reaction equation, which makes obsolete the *a priori* assumption of complete CH_4 consumption in the model domain applied in the C07 model. The refinement now also provides the opportunity to account for CH_4 flux from below (*i.e.*, due to CH_4 production in soil, if present) and to set a minimum methane concentration threshold at which methanotrophy can occur in the soil column. In addition, MeMo revisits and improves R99 and C07 model formulations to incorporate advances in the mechanistic understanding of soil methanotrophy that have resulted from availability of new data. Finally, MeMo utilizes for the first time data for atmospheric N deposition and N input from fertilizers to explore more accurately the effect of land-use and land-use changes on the global CH_4 sink. This chapter presents a comprehensive description of the new model, a comparison of MeMo with the R99 and C07 models, and a critical discussion of model formulations and assumptions based on observational data.

2.2 Model Description

The following sections provide a detailed description of MeMo in the context of existing global soil CH_4 uptake. Table 2.1 provides a summary of all terms, names and units used in the model description section, while Table 2.2 contains a short summary of the four global CH_4 uptake models based on the P96 family.

Table 2.1 Terms, names and units used in the model description section

Terms	Name	Units
CH_4	CH_4 concentration	mg m^{-3}
J_{CH4}	CH_4 flux uptake	mg CH_4 m^{-2} mo^{-1}
C_{CH4}	Atmospheric CH_4 concentration	ppb
CH_4 min	CH_4 threshold	ppb
F_{CH4}	CH_4 flux through L	mg CH_4 m^{-2} mo^{-1}
z	Depth in the soil profile	cm
L	Depth at CH_4 concentration is fully depleted into the soil	cm
D_{CH4}	Diffusion coefficient of CH_4 into soil	cm^2 s^{-1}
k_d	CH_4 oxidation activity	s^{-1}
$D_{0CH4} = 0.196$	CH_4 diffusion in free air at standard temperature and pressure STP= 0°C and 1 atm pressure	cm^2 s^{-1}
G_T	Soil temperature response	°C
G_{soil}	Soil structure response	dimensionless
Φ	Total pore volume	cm^3 cm^{-3}
ρ	Bulk density	cm^{-3} g^{-1}
$d = 2.65$	Soil particle density	g cm^{-3}

Φ_{air}	Air-filled porosity	$cm^3\ cm^{-3}$
θ	Soil water content	%
w	Saturation soil water potential	MPa
b	Clay soil content factor	dimensionless
f_{clay}	Clay soil content	%
k_0	Base oxidation rate constant for uncultivated moist soil at 0°C	s^{-1}
r_{SM}	Microbial CH_4 oxidation, soil moisture response	dimensionless
r_T	Microbial CH_4 oxidation, temperature response	dimensionless
r_N	Microbial CH_4 oxidation, nitrogen response	dimensionless
N_{soil}	Nitrogen deposition into soil	$g\ N\ m^{-2}\ mo^{-1}$
$\alpha = 0.33$	Average coefficient of N deposition inhibition	$\%\ mol\ N^{-1}$

2.2.1 Conservation Equation

The general, one-dimensional mass conservation equation for CH_4 in soil is given by:

$$\frac{\partial CH_4}{\partial t} = -\frac{\partial J_{CH4}}{\partial_z} + \sum R \quad (1)$$

Where J_{CH4} denotes the flux of CH_4 and ΣR is the sum of all production and consumption processes that affect CH_4 concentrations in soil. The flux J_{CH4} in the soil is generally controlled by diffusion. Consequently, the P96 model assumes that global uptake of atmospheric CH_4 by soil is diffusion limited and thus describes the soil CH_4 sink as a purely diffusive process (*i.e.*, $\sum R = 0$). However, CH_4 is consumed by microbial activity in the soil and the simplified diffusion model may thus underestimate total uptake of CH_4. Consequently, R99 extended the diffusion model by explicitly accounting for microbial oxidation of CH_4 through a first order rate expression. The resulting diffusion- reaction equation forms the basis of the R99 model, the C07 model and MeMo:

$$\frac{\partial CH4}{\partial t} = -D_{CH4}\ \frac{\partial^2 CH_4}{\partial z^2} + k_d * CH_4 \quad (2)$$

Where D_{CH4} is the CH_4 diffusion coefficient and k_d the first-order rate constant for microbial CH_4 oxidation. Under steady-state conditions (*i.e.*, $\partial CH_4/\partial t=0$), soil CH_4 uptake is controlled by the balance between diffusion of CH_4 into soil and the rate of microbial CH_4 oxidation. Hence, accurate characterization of D_{CH4} and k_d is essential for a robust quantification of CH_4 uptake by soil.

2.2.2 Solution of Reaction-Transport Equation

The R99 model solved Eq. (2) semi-numerically by (i) assuming steady-state, (ii) numerically approximating the diffusion term similar to the approach applied in the P96 model (Table 2.2, Eq. 11), and (iii) assigning CH_4 oxidation exclusively to a distinct soil layer of thickness ϵ at depth z_d = 6 cm (Table 2.2, Eq. 12). However, CH_4 consumption can occur throughout a soil profile and thus Eq. (12) (Table 2.2) may either overestimate or underestimate the CH_4 sink.

In the C07 model, Eq. (2) was solved analytically, providing a more accurate and mathematically robust estimate of CH_4 uptake Eq. (13) (Table 2.2). Assuming steady-state conditions and constant D_{CH4} and k_d throughout the soil profile, integration of Eq. (2) provides a general solution for determining CH_4 concentration at depth z in soil:

$$CH_4(z) = A * exp\left(-\sqrt{\frac{k_d}{D_{CH4}}}z\right) + B\ exp\left(\sqrt{\frac{k_d}{D_{CH4}}}z\right) \quad (3)$$

Where A and B are integration constants that can be determined by setting upper and lower boundary conditions for the soil profile. The concentration of CH_4 at the soil-atmosphere interface is defined by the atmospheric concentration of CH_4 (C_{CH4}) and thus, a Dirichlet boundary (*i.e.*, fixed concentration) is applied at the upper boundary. Conditions at the lower boundary are more challenging to ascribe because the soil depth at which atmospheric CH_4 is completely consumed is not known *a priori*.

2.2.2.1 Negligible CH_4 flux through the lower boundary (C07 Solution)

The C07 model circumvents the problem by applying a homogenous Neumann (no-flux) condition at the lower model boundary: $\frac{dCH_4}{d_z}|_{z->\infty} = 0$

The application of this boundary condition allows derivation of the integration constants $A = C_{CH4}$ and $B = 0$, which simplifies Eq. (3) to:

$$CH_4(z) = C_{CH4} * exp\left(-\sqrt{\frac{k_d}{D_{CH4}}} * z\right) \quad (4)$$

The diffusive uptake of atmospheric CH_4 at the soil-atmosphere interface can then be calculated using the derivative of Eq. (4) at $z = 0$:

$$J_{CH4} = -D_{CH4} * \frac{dCH4}{d_z}|_{z=0} = D_{CH4} * C_{CH4} * \sqrt{\frac{k_d}{D_{CH4}}} = \quad C_{CH4}\sqrt{D_{CH4}k_d} \qquad (5)$$

This formulation of soil uptake of CH_4 is the simplest analytical solution to Eq. (2). It represents an improvement from the semi-numerical representation used in the R99 model and enables complete consumption of CH_4 to be accounted for within the soil; however, the homogeneous Neumann boundary condition applied here is only an approximation, which is not generally valid. The simulation will not be influenced if the Neumann boundary is infinitely far from the consumption depth of CH_4 and thus, the corresponding Neumann boundary condition can be neglected. However, if this is not the case, it will result in simulation error.

2.2.2.2 Complete consumption of CH_4 at an a priori unknown depth L (MeMo solution)

Therefore, we adopted an approach similar to model C07 but one that is generally valid. We assume that methanotrophy consumes atmospheric CH_4 in the soil until CH_4 reaches a threshold ($CH_4\,(L) = CH_4\,min$) that can be imposed based on biological limits ($CH_4\,min$ = 100 ppb) or when CH_4 is fully depleted ($CH_4\,min$ = 0). The integration constants in Eq. (3) thus become:

$$A = -\frac{C_{CH4} * exp\left(\sqrt{\frac{k_d}{D_{CH4}}}L\right) - CH4min}{\left[exp\left(-\sqrt{\frac{k_d}{D_{CH4}}}L\right) - exp\left(\sqrt{\frac{k_d}{D_{CH4}}}L\right)\right]} \qquad (6)$$

$$B = \frac{-CH4\,min + C_{CH4} * exp\left(-\sqrt{\frac{k_d}{D_{CH4}}}L\right)}{\left[exp\left(-\sqrt{\frac{k_d}{D_{CH4}}}L\right) - exp\left(\sqrt{\frac{k_d}{D_{CH4}}}L\right)\right]} \qquad (7)$$

In addition to the concentration condition $CH_4\,(L) = CH_4\,min$, a flux condition also is imposed on the lower boundary in order to determine depth L: $-D_{CH4} * \frac{dCH4}{d_z}|_{z=L} = F_{CH4}$

Where F_{CH4} denotes a potential CH_4 flux across the lower boundary that can be specified (*i.e.*, $CH_4\,(L) = CH_4\,min$) or set equal to zero (*i.e.*, $CH_4\,(L) = 0$). The unknown depth L is then calculated by substituting the derivative of Eq. (3) into the expression for the lower boundary condition:

$$-D_{CH4} * \frac{dCH4}{dz}|L = -D_{CH4} * \left(A\left(-\sqrt{\frac{k_d}{D_{CH4}}}\right) * exp\left(-\sqrt{\frac{k_d}{D_{CH4}}}L\right) + B\sqrt{\frac{k_d}{D_{CH4}}} * exp\left(\sqrt{\frac{k_d}{D_{CH4}}}L\right)\right) = F_{CH4} \qquad (8)$$

Rearranging Eq. (8) and finding its root allows for the determination of the initially unknown depth L when $CH_4(L) = CH_4\,min$:

$$\mathbf{0} = -\boldsymbol{D_{CH4}}\sqrt{\frac{k_d}{D_{CH4}}}\,\frac{\left(2\,C_{CH4}-CH4min*exp\left(-\sqrt{\frac{k_d}{D_{CH4}}}L\right)-CH4min*exp\left(\sqrt{\frac{k_d}{D_{CH4}}}L\right)\right)}{\left[exp\left(-\sqrt{\frac{k_d}{D_{CH4}}}L\right)-exp\left(\sqrt{\frac{k_d}{D_{CH4}}}L\right)\right]} - \boldsymbol{F_{CH4}} \tag{9}$$

Once L is known total CH_4 uptake can be calculated from:

$$J_{CH4} = -D_{CH4} * \frac{dCH4}{d_z}|_{z->z=0} = -D_{CH4}\left(-A\sqrt{\frac{k_d}{D_{CH4}}} + B\sqrt{\frac{k_d}{D_{CH4}}}\right) \tag{10}$$

Where A and B are defined by Eqs. (6) and (7). When L tends to infinity Eq. (10) is equivalent to the model C07 solution; however, Eq. (10) also allows for (i) complete consumption of CH_4 within the soil interval, (ii) influx of CH_4 from beneath the soil profile (*e.g.*, from thawing permafrost or production of CH_4 in oxygen-depleted microsites in soil), and (iii) a minimum CH_4 concentration at which methanotrophy can occur in the soil column.

Figure 2.1 illustrates CH_4 soil profiles and the penetration depth of CH_4 into soil, L, for different k_d values, $F_{CH4} = 0$ and $D_{CH4} = D_{0CH4}$ (diffusivity in free air) (Table 2.1). It is expected that L will vary spatially depending on local k_d, D_{CH4} and soil properties.

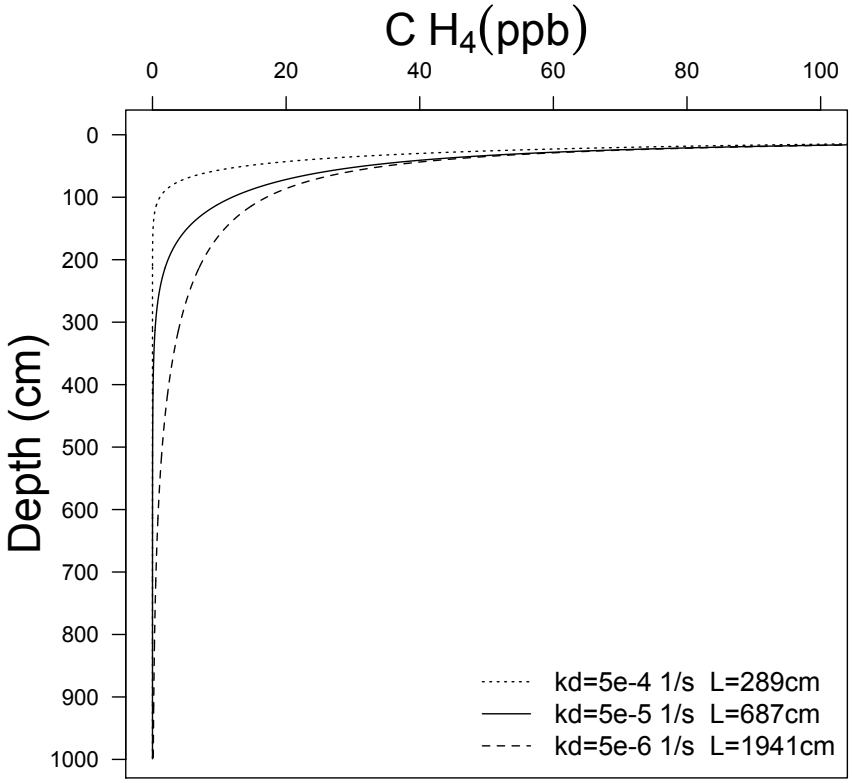

Figure 2.1 Graphic description of parameter L. Computational solution of Eq. (9) for different values of k_d (s^{-1}). Parameter L is defined as the depth where $CH_4\ min = 0$, assuming complete removal of CH_4 in soil pore spaces.

Table 2.2 Descriptions of four soil methanotrophy global models.

Model / Study	Description	CH_4 uptake calculation (J_{CH4})	Eq.
P96 Potter et al. (1996)	Model based on Fick's first law. The calculation of the uptake flux is approximated numerically and based on the diffusion of CH_4 into soil.	$J_{CH4} = D_{CH4}\frac{\Delta C_{CH4}}{\Delta_z}$	(11)
R99 Ridgwell et al. (1999)	R99 extends the P96 model by including an explicit term for microbial oxidation of CH_4 in soil. The uptake flux is approximated numerically, using Fick's first law and adopting a first order rate law for microbial oxidation, assuming that oxidation occurs in a thin ϵ cm layer located at 6 cm depth.	$J_{CH4} = \frac{C_{CH4}D_{CH4}}{z_d}\left(1 - \frac{D_{CH4}}{D_{CH4} + k_d z_d}\right)$	(12)

C07 Curry (2007)	C07 adopts the diffusion-reaction equation that underlies R99. However, C07 solves the equation analytically (as opposed to semi-numerically). The model also improves representation of soil moisture influence on the microbial oxidation rate. C07 refines methanotrophy response at subzero temperatures on the basis of observations.	$J_{CH4} = C_{CH4} r_N r_w \sqrt{D_{CH4} k_d}$	(13)
MeMo This study	Incorporates a general mathematical description of CH_4 uptake flux, allowing for complete consumption of CH_4 at an initially unknown depth L and CH_4 flux through the lower boundary. Refines representation of the influence of soil moisture, temperature and nitrogen deposition on CH_4 oxidation.	$J_{CH4} = -D_{CH4}\left(-A\sqrt{\frac{k_d}{D_{CH4}}} + B\sqrt{\frac{k_d}{D_{CH4}}}\right)$	(10)

MeMo is based on the more general solution (Eq. (10)) and uses local methanotrophy rates (k_d) and diffusion coefficients (D_{CH4}) based upon soil conditions to determine CH_4 penetration depths (L). Additionally, Eq. (9) allows one to set a minimum CH_4 concentration if this parameter is known. In this case, we assume a minimum of 0 or complete consumption. We assume no *in situ* production of CH_4 or upward CH_4 flux from below (*i.e.*, $F_{CH4} = 0$) because of a scarcity of field data for model validation. However, a flux from below can be employed in MeMo to enable a more comprehensive quantification of soil CH_4 uptake that also potentially accounts for consumption of upward migrating CH_4 and autochthonous CH_4 produced in oxygen-depleted microsites of finely textured soil.

2.3 Parameters

The rate of CH_4 uptake by soil is controlled by the balance between gaseous diffusion of atmospheric CH_4 into soil and the rate of CH_4 oxidation by methanotrophic bacteria as described by Eq. (14) and Eq. (20), respectively. Thus, D_{CH4} and k_d are key parameters and accurate characterization of their values is essential for robust quantification of the soil CH_4 sink.

2.3.1 Soil CH_4 Diffusivity, D_{CH4}

Similar to the R99 and C07 models, D_{CH4} in MeMo is determined from the diffusivity of CH_4 in free air (D_{0CH4}; Table 2.1) adjusted for the influence of temperature (G_T) and soil structure (G_{soil}):

$$D_{CH4} = D_{0CH4} * G_T * G_{soil} \quad (14)$$

The gaseous diffusion coefficient of CH_4 in soil increases linearly with temperature T (°C) (Potter et al., 1996) according to the relationship:

$$G_T = 1.0 + 0.0055\,T\ (°C) \quad (15)$$

The soil structure factor (G_{soil}) accounts for the effects of pore size, connectivity and tortuosity on gaseous diffusion and is determined according to the parameterization of Moldrup et al. (1996; 2013):

$$G_{soil} = \Phi^{4/3}\left(\frac{\Phi_{air}}{\Phi}\right)^{1.5+3/b} \quad (16)$$

Where Φ is total pore volume ($cm^3\ cm^{-3}$), Φ_{air} is air-filled porosity ($cm^3\ cm^{-3}$) and b is a scalar that accounts for soil structure. Total pore volume is defined as a function of bulk density ρ ($g\ cm^{-3}$) and average particle density d (Table 2.1) (Brady et al., 1999):

$$\Phi = 1 - \left(\frac{\rho}{d}\right) \quad (17)$$

The scalar b in Eq. (16) is calculated as a function of soil clay content (f_{clay}; %) as proposed by Saxton et al. (1986):

$$b = 15.9\,f_{clay} + 2.91 \quad (18)$$

Air-filled porosity (Φ_{air}) is determined from the difference between total pore volume and soil water content θ (%):

$$\Phi air = \Phi - \theta \quad (19)$$

2.3.2 Rate Constant for CH_4 Oxidation, k_d

The CH_4 oxidation rate (k_d) is defined as the base oxidation rate constant (k_0) for an uncultivated moist soil at 0°C scaled by three factors to account for the influence of soil moisture (r_{SM}), soil temperature (r_T), and nitrogen content (r_N):

$$k_d = k_0 * r_{SM} * r_T * r_N \quad (20)$$

The R99 and C07 models used a similar equation to estimate k_d but without the r_N parameter, opting instead to employ intensity of agricultural activity as a proxy to account for the inhibitory effects of N deposition on soil methanotrophy. Moreover, model C07 excluded r_N from the k_d formulation and used a N deposition term to modify total CH_4 uptake flux (Table 2.2, Eq. 13), which results in a larger N inhibition effect. The approach employed in MeMo is to use N deposition data directly to modify k_d.

2.3.2 Base Oxidation Rate Constant, k_0

The base oxidation rate constant (k_0) is a key parameter that exerts significant control on k_d and thus the estimated CH_4 uptake flux. For example, a 10-fold change in k_0 (and thus k_d) leads to a 3-fold decrease in the depth L at which CH_4 is fully depleted from soil pores (Fig. 2.1) and a ~3-fold increase in total uptake of CH_4 (Fig. 2.2).

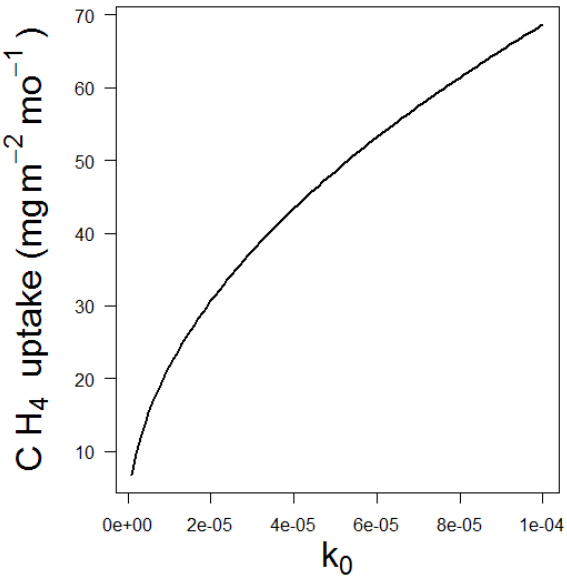

Figure 2.2 Graphic description of k_0. Total CH_4 uptake for different values of k_0 (s^{-1}), assuming a constant value of $D_{CH4} = D_{0CH4}$ and no modification by soil temperature, moisture or nitrogen deposition.

Rate constants can be defined either on the basis of theoretical considerations or through site-specific field and laboratory observations. Rates of soil microbial processes, such as CH_4 oxidation, are controlled by microbial biomass dynamics and community structure, and, thus a complex array of environmental factors, including temperature, substrate (CH_4) concentration, land use, moisture, pH and soil type (Ho et al., 2013). The influence of these environmental factors on microbial CH_4 oxidation rates is not well characterized and thus all factors are not explicitly represented in models. Consequently, apparent rate constants implicitly account for some environmental factors via fitting field observations or laboratory experiments, resulting in parameter values that may be more environment- and model-specific. A possible limitation of such an approach is reduced transferability and predictive capacity in other environments or from a regional to global scale. For example, Ridgwell et al. (1996) derived a single global estimate of $k_0 = 8.7 \times 10^{-4}$ s^{-1} by fitting Eq. (12) to 13 measured values of J_{CH4}, D_{CH4} and soil temperature from four different studies. In contrast, Curry (2007) estimated a global k_0 of 5.0×10^{-5} s^{-1} based upon fitting Eq. (13) to a five-year time series of J_{CH4} and soil temperature, moisture and CH_4 flux measurements from a single site in Colorado (Mosier et al., 1996). The order of magnitude difference in k_0 between the R99 and C07 models illustrates the potential model-specific nature of parameter values derived from experimental and observational data, as well as the limits and challenges for transferability. Soil methanotrophy is not unique in this regard and parameterization of microbially mediated processes remains a common problem more generally in modelling approaches (*e.g.*, Arndt et al., 2013; Bradley et al., 2016).

Parameterization of k_0 in MeMo has been refined using time-series data recently published by Luo et al., (2013), which consist of daily soil CH_4 uptake rates and temperature and soil moisture data from three contrasting environments: temperate forest (Hoglwald Germany), tropical rainforest (Bellenden Ker Australia) and steppe (Inner Mongolia, China). The data sets were used to explore potential variations in apparent k_0 values in different environments, including comparison with k_0 values from models R99 and C07; however, the uncertainty of this value could not be characterized due to a dearth of available observational data. Data from each site were interpolated according to Eq. (10) to derive an apparent k_0 value for each biome. The k_0 values for temperate forest and steppe are similar to the k_0 value employed in the C07 model; however, the apparent k_0 for tropical forest is approximately three times smaller than the model C07 k_0 value. The three newly derived k_0 values were employed in MeMo for their respective biomes and the k_0 value from the C07 model ($k_0 = 5.0 \times 10^{-5}$ s^{-1}) was used for all other regions for which no biome specific k_0 values exist (Table 3). Similar k_0 values of 5.0×10^{-5} s^{-1} for temperate forest, steppe and short grass steppe indicate that this

magnitude of k_0 is appropriate for many ecosystems. Yet, apart from the tropical wet forest, the data clearly indicate additional controls and the use of $k_0 = 1.6 \times 10^{-5}$ s^{-1} will thus prevent an overestimation of simulated fluxes. Nevertheless, further research is required to better characterize this key parameter.

Table 2.3 k_0 values from models R99 and C07 and new k_0 values employed in MeMo that were determined based upon temperate forest, tropical forest and steppe data from Luo et al. (2013).

Model	Biome	k_0 (s^{-1})
R99	Global	8.7×10^{-4}
C07	Global	5.0×10^{-5}
MeMo	Temperate forest	4.0×10^{-5}
	Tropical forest	1.6×10^{-5}
	Steppe	3.6×10^{-5}
	Other ecosystems	5.0×10^{-5}

2.3.3 Soil Moisture Factor, r_{SM}

Both low and high soil moisture levels can negatively impact soil uptake of atmospheric CH_4 (Schnell and King, 1996; von Fischer et al., 2009). Scarcity of soil water generally inhibits soil microbial activity while excessive moisture attenuates gas diffusion, limiting entry of atmospheric CH_4 and O_2 into soil (Burke et al., 1999; McLain et al., 2002; McLain and Ahmann, 2007; West et al., 1999).

Models R99 and C07 incorporated parameters to address the limiting effects of low soil moisture levels on CH_4 uptake fluxes. The R99 model applied a soil moisture factor adopted from Potter et al. (1986) where r_{SM} was calculated as a proportional ratio of precipitation (P) plus soil moisture (SM) divided by potential evapotranspiration (ET; Table 2.4, Eq. (21)). It was assumed that r_{SM} decreases linearly when $(P+SM)/ET$ is less than one. The C07 model modified the response of soil methanotrophy to moisture using an empirical water stress parameterization and soil water potential based on findings from Clapp and Hornberger (1978) (Table 2.4, Eq. (22)). A consequence of that approach is that r_{SM} decreases logarithmically to zero at an absolute soil water potential of $w < 0.2$ MPa (Fig. 2.3).

In MeMo, soil moisture (%) is used to calculate r_{SM} and a formulation similar to the C07 model is used for low soil moisture values. A threshold of <20% soil moisture is applied because that value corresponds to optimum conditions for CH_4 oxidation in soil (Castro et al.,

1995; Whalen and Reeburgh, 1996) and because inclusion of a water stress parameter better captures CH_4 uptake flux in dry ecosystems (Fig. 2.3; Curry, 2007).

Establishing parameters to quantify the impact of excess moisture on soil methanotrophy has proven more challenging. The C07 model relied upon soil pore space characteristics in factor G_{soil} (Eq. (16)) to account for decreased gas diffusion and limitation of k_d at high soil moisture content. However, attenuation of gas diffusion is only one impact of high soil water content and it is necessary also to account for the inhibitory effects of excessive moisture on k_d (Boeckx & Van Cleemput, 1996; Dasselaar et al., 1998; Visvanathan et al., 1999). Soil moisture content >20% reduces CH_4 uptake due to a restricted diffusion of CH_4 and supply of O_2. The R99 and C07 models assume that microbial CH_4 oxidation remains active at a soil moisture content of 80%, an assumption that contradicts field investigations, which show that CH_4 uptake decreases rapidly at soil moisture levels >50% (Dasselaar et al., 1998). Thus, the soil moisture factor employed in MeMo also accounts for limitation of microbial CH_4 oxidation at a soil moisture content >20% after which rates of CH_4 uptake begin to decrease (Adamsen & King, 1993; Visvanathan et al., 1999). The r_{SM} factor used in MeMo was determined by fitting a Gaussian function to laboratory experimental data (Table 2.4, Eq. (23); Fig. 2.3a), following the approach of Del Grosso et al. (2000). The mean r_{SM} and standard deviation determined using this approach were 0.2 ± 0.2.

Table 2.4 Model R99, C07 and MeMo formulations for r_{SM} response.

Model	Formulation		Eq.	Variable definitions
R99	$r_{SM} = 1$ for P+SM/ET	for p>1	(21)	P=precipitation SM=soil moisture stored at 30 cm depth ETp=potential evapotranspiration
	$r_{SM} = \mathrm{P} + \mathrm{SM/ETp}$	for P+SM/ET p≤1		
C07	$r_{SM} = 1$	for w<0.2MPa	(22)	w=saturation soil water potential
	$r_{SM} = \left[1 - \frac{log_{10}w - log_{10}(0.2)}{log_{10}(100) - log_{10}(0.2)}\right]^{0.8}$	for w≥0.2≤100MPa		
MeMo	$r_{SM} = \left[1 - \frac{log_{10}\frac{1}{SM} - log_{10}(0.2)}{log_{10}(100) - log_{10}(0.2)}\right]^{0.8}$	for SM<0.2	(23)	SM=soil moisture
	$r_{SM} = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{SM-0.2}{0.2}\right)^2}$	for SM>0.2		

A soil moisture factor (r_{SM}) was calculated for each set of observational data from independent field sites (Appendix A, Table A2.1) based upon an optimum rate of CH_4 uptake occurring at a soil moisture content of 20% (r_{SM}= 1). The remaining r_{SM} values were computed as a linear ratio of the CH_4 uptake rate at 20% water content. Figure 2.3b illustrates the pattern of response in methanotrophy rates to changes in soil moisture content in the R99, C07 models and MeMo and the net effect on CH_4 uptake fluxes across a range of absolute soil moisture levels used to force parameter r_{SM}. The CH_4 uptake fluxes were calculated by varying soil moisture content while holding constant all other environmental parameters (temperature, C_{CH4} and N_{dep}). The R99 and C07 models both predict greater CH_4 uptake fluxes than MeMo at soil moisture contents >20% with the R99 model yielding the highest flux rates; however, the C07 model and MeMo yield similar CH_4 uptake rates for much of the soil moisture range. Reduction of CH_4 uptake flux at high soil moisture levels due to attenuation of gas diffusion cannot be managed solely through the term G_{soil} (*i.e.*, reduction in free pore space). MeMo also accounts for inhibition of microbial CH_4 oxidation rates at elevated soil moisture content, predicting lower CH_4 uptake flux as a result of more realistic r_{SM} values determined from the Gaussian response observed in field data from three different global biomes (Luo et al*.,* 2013).

2.3.4 Temperature Factor, r_T

Temperature exerts an important influence on rates of microbial processes and consequently all models parameterize for the effects of temperature on soil methanotrophy. The R99 model employs a Q_{10} function derived from experimental data with a Q_{10} factor of 2 change over the temperature interval 0 to 15°C. The model assumes that bacterial methanotrophy ceases at temperatures <0°C (Table 2.5, Eq. (24)). The C07 model adopts the same Q_{10} factor as R99 for temperatures >0°C but employs a different response below 0°C. Soil water generally does not freeze at a surface temperature of 0°C and observations from cold regions provide ample evidence for the presence of methanotrophic activity at temperatures <0°C (Vecherskaya et al. 2013). The C07 model allows for a parabolic decrease of methanotrophy rates from 0 to -10°C (Table 2.5, Eq. (25)) based upon observations of CH_4 uptake in soil at subzero temperatures (Del Grosso et al., 2000).

Parameterization of a temperature factor (r_T) is revisited in MeMo based upon availability of new experimental data for soil from different biomes (Appendix A, Table A2.2). A Q_{10} factor having a value of 1.95 was determined for the temperature interval 0 to 15 °C by curve fitting and minimizing linear errors ($r^2 = 0.75$, $p=1.9\ e^{-11}$; Table 2.5, Eq. (26)). The factor r_T was determined by using the observed CH_4 uptake flux at 10°C at each site as the base of

the Q_{10} function (Fig. 2.3c). An exponential decrease in CH_4 uptake flux was assigned to the temperature range 0 to -5°C as recommend by Castro et al. (1995) and Del Grosso et al. (2000). Moreover, the amount of frozen soil increases exponentially with decreasing temperatures (Low et al., 1968) and consequently, CH_4 uptake also should decline exponentially.

Table 2.5 Model R99, C07 and MeMo formulations for r_T response.

Model	T<0°C	T≥0°C	Eq.
R99	$r_T = 0$	$r_T = \exp(0.0693T - 8.56x10^{-7} T^4)$	(24)
C07	$r_T = (0.1T+1.0)^2$ ifT>-10°C	$r_T = \exp(0.0693T - 8.56x10^{-7} T^4)$	(25)
MeMo	$r_T = 1/\exp(-T)$	$r_T = \exp(0.1515+0.05238T - 5.946x10^{-7} T^4)$	(26)

The pattern of change in the r_T factor and CH_4 uptake flux for the temperature range -10 to 60°C is shown in Fig. 2.3d. The CH_4 uptake fluxes shown were calculated by varying temperature while holding other environmental factors constant (*i.e.*, soil moisture, N deposition or agricultural land use, and C_{CH4}). All models exhibit an optimum in CH_4 uptake at 25°C characterized by a maximum r_T and CH_4 oxidation rate. The key differences between models are the behavior of r_T at temperatures below 0°C and the amplitude of response curves. The R99 model assumes that methanotrophic activity ceases at 0°C and consequently, CH_4 uptake rates decrease sharply at that temperature. In contrast, models C07 and MeMo both allow for methanotrophy at temperatures <0°C. In general, the exponential decrease of r_T employed in MeMo more closely resembles natural patterns of soil methanotrophy at subzero temperatures than the parabolic decline employed in the C07 model consistent with observations reported by Castro et al. (1999) and Del Grosso et al. (2000). Although our parameterization yields a fit similar to C07 to the limited observations available at temperatures <0°C the r_T used in MeMo provides a simpler solution because it does not require multiple conditions to be met. In contrast, the C07 parameterization increases parabolically at temperatures <-10º C, which requires an additional condition to be incorporated into the model to prevent increased rates of CH_4 uptake at very low temperatures. Soil CH_4 uptake fluxes predicted by the C07 model are greater than those calculated using MeMo because of the different parameterization at temperatures <0°C. Finally, the amplitude of the temperature response curve is greater and similar in models C07 and MeMo compared to model R99, in particular, at temperatures >25°C as a result of differences in the formulation and solution for CH_4 uptake flux (Fig. 2.3d).

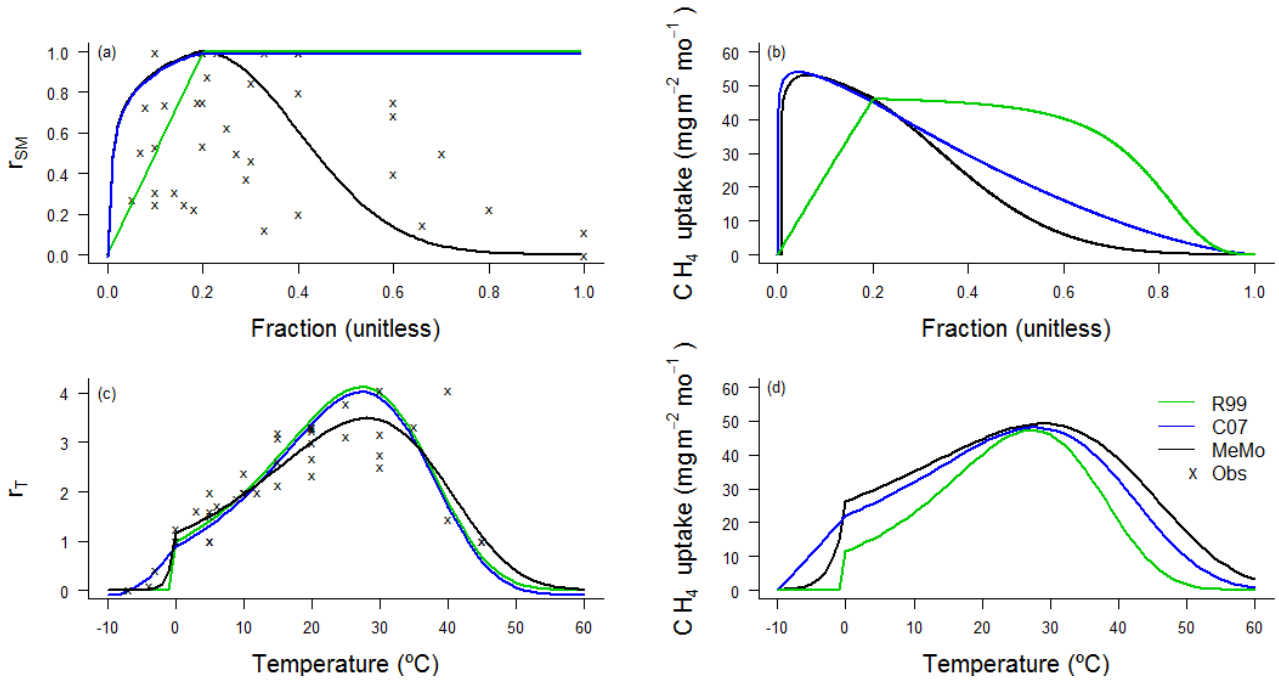

Figure 2.3 CH_4 uptake response factors (a, c) and uptake fluxes (b, d) as a function of soil moisture (r_{SM}) and temperature (r_T). Observations (shown as crosses) (r_{SM}, Appendix A, Table A2.1; r_T, Appendix A, Table A2.2), MeMo (black line), C07 (blue line) and R99 (green line).

2.3.5 Nitrogen Deposition factor, r_N

The effect of nitrogen (N) deposition on CH_4 uptake is not as well constrained as the effects of temperature and soil moisture. In general, field observations have shown that CH_4 consumption rates and thus, uptake fluxes decrease with N additions (Aronson & Helliker, 2010; Butterbach-Bahl & Papen, 2002; Steinkamp et al., 2001). Different processes have been suggested to explain this negative effect. Firstly, methanotrophs and ammonia oxidizers are capable of switching substrates (although the latter microorganisms typically consume N compounds preferentially if available) and therefore the presence of N compounds reduces CH_4 consumption (Bradford et al., 2001; Gulledge & Schimel, 1998; Phillips et al., 2001; Wang & Ineson, 2003; Whalen, 2000). In addition, intermediate and end products from methanotrophic ammonia oxidation (*i.e.*, hydroxylamine and nitrite) can be toxic to methanotrophic bacteria (Bronson and Mosier, 1994; MacDonald et al., 1996; Sitaula et al., 2000). Finally, large amounts of mineral fertilizers (*i.e.*, ammonium salts) can induce osmotic stress in methanotrophs inhibiting CH_4 consumption (Whalen, 2000). However, other studies suggest a positive effect of N fertilization on CH_4 oxidation rates. One of the mechanism invoked to explain the positive effect is a stimulation of nitrifying bacteria to consume CH_4 by increased inputs of N due to an improvement in living conditions (Cai & Mosier, 2000; De Visscher &

Cleemput, 2003; Rigler & Zechmeister-Boltenstern, 1999). The positive effect of N addition on CH_4 oxidation rates has been observed primarily under experimental conditions and also greatly depends on the local microbial community structure. Therefore, we assumed that N has an inhibitory effect on uptake of atmospheric CH_4 in all scenarios.

The C07 and R99 models both account for the negative effect of N inputs on CH_4 uptake fluxes via the factor r_N. In model R99, r_N directly affects k_d while in model C07 r_N directly modifies the uptake flux. Both models parameterize the negative effect of N inputs on CH_4 oxidation rates as a function of agricultural intensity (as a fraction of area) as a proxy for fertilizer application (Table 2.6, Eq. (27)). However, the mathematical description of r_N used by models R99 and C07 does not account for the enhanced N deposition by anthropogenic activity or direct N input via fertilizers because its global distribution was not well known at the time of model development. Here, we suggest a mathematical description of r_N that accounts for all anthropogenic N input sources: fossil fuel combustion, biomass burning and fertilizer application (Lamarque, 2013; Nischina et al., 2017).

The computation of r_N in MeMo is a function of: i) the inhibitory effect on CH_4 uptake, and ii) the distribution and amount of N input in soil (Zhuang et al., 2013). We estimated the percent reduction of CH_4 uptake per mol of N added based on field and laboratory observations (Appendix A, Table A2.3). We determined an average inhibition α of 0.33% mol N^{-1} based on the mean uptake reduction per mol of N added. The N response function r_N was governed by Eq. (29):

$$r_N = 1 - (N_{soil} * \alpha) \qquad (29)$$

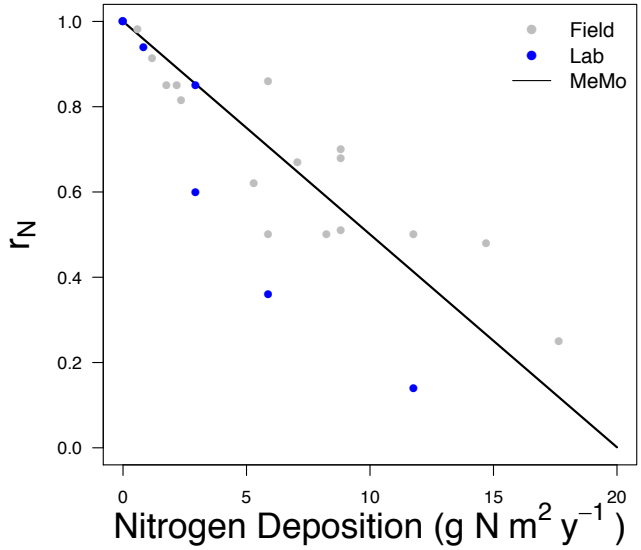

Figure 2.4 CH_4 uptake response as a function of nitrogen deposition and fertilizer application factor r_N. The linear fit (black line) is based on observations from field (long-term) and laboratory measurements (gray and blue dots; Appendix A, Table A2.3).

In cases where entry of N into soil is limited by bulk density ρ, ninety percent of N compounds tend to remain at depths $z <= 5$ cm before exponentially decreasing in concentration with depth (Schnell & King, 1994). Thus, N_{soil} was calculated as N input (kg N ha^{-1} y^{-1}) divided by ρ at $z = 5$ cm:

$$N_{soil} = \frac{Ndep+Nfert}{(\rho * z)} \quad (30)$$

Figure 2.4 shows the change in r_N in relation to N input rate and the form of Equation (29).

Table 2.6 Model R99, C07 and MeMo formulations for r_N response.

Model	Formulation	Eq.	Driving data
R99	$r_N = 1.0 - (0.75 \times I)$	(27)	I = fractional intensity of cultivation
C07	$r_N = 1.0 - (0.75 \times I)$	(28)	I = fractional intensity of cultivation (r_N outside of k_d parameterization)
MeMo	$r_N = 1-(N_{soil}) * \alpha$	(29)	$N_{soil} = \frac{Ndep+Nfert}{(\rho * z)}$ (30)

2.4 Model implementation

MeMo was implemented in R (version 3.0.1) and simulations were carried out with a spatial resolution of 1°x1° and a monthly temporal resolution for the period between 1990 and 2009. The model code, a simple model case study for year 2000 and output for 1990-2009 are available as a supplement to this manuscript. To enable model-model comparisons and assess the combined effect of all refinements introduced in MeMo on the global CH_4 uptake flux estimate, the R99 and C07 models also were implemented in R at identical spatial and temporal resolutions and forced using the same driving data.

2.4.1 Forcing data

MeMo and the C07 and R99 models were forced using global monthly observations of soil moisture, temperature, atmospheric CH_4 concentration, N deposition, soil bulk density, and clay content for the period 1990-2009. Information about data sources and maps of the forcing data are provided in Appendix B.

Satellite observations of soil moisture at a spatial resolution of 1x1° and a monthly temporal resolution are available for the period 1990-2009 from Dorigo et al. (2011); however, the data set contains gaps in some regions (*e.g.*, in areas of high-density vegetation). The use of MeMo as a predictive tool to estimate the past and future global CH_4 soil sink relies strongly on the use of soil moisture from standard climate models, such as output from land surface models or Dynamic Global Vegetation Models (DGVMs). Therefore, gaps in the Dorigo et al. (2011) data set were filled using soil moisture data from an ensemble of 9 DGVMs (TRENDY; Sitch et al., 2015), using the variable mean soil moisture (mrso) at near surface ~20-50 cm depth. The R99 model parameterizes the effect of soil moisture on CH_4 uptake fluxes as a function of precipitation and evaporation and therefore, R99 was forced using monthly precipitation (CRU3.1; Harris et al., 2014) and evapotranspiration (TRENDY; Sitch et al., 2015) data. Temperature forcing was constrained by global data sets for surface temperature as a proxy for soil temperature (CRU3.1; Harris et al., 2014). Monthly mean global atmospheric CH_4 concentrations multiplied by the latitudinal atmospheric CH_4 gradient were calculated from Rigby et al. (2008). The N deposition data were obtained from an atmospheric chemical transport model embedded in an Earth System Model (Lamarque et al., 2013) and the N input via fertilizers was obtained from Nischina et al. (2017). Because the R99 and C07 models express the influence of N on CH_4 uptake fluxes as a function of fraction agricultural area (see section 2.3.6), R99 and C07 were forced using annual global gridded land-use change data from Hurtt et al. (2011). Finally, global gridded observations for bulk density and clay content were taken from Shangguan et al. (2014).

Areas that have less than 0.5% average annual soil moisture content were masked (e.g., Sahara Desert) because it was assumed CH_4 uptake is negligible under such conditions. If the areas were left unmasked, then MeMo would overestimate CH_4 uptake across the regions due to high temporal variability in the driving data (*e.g.*, a month with no moisture followed by a month with >20%). Irregular short-lived precipitation events in deserts lead to unreliable estimates of soil uptake of atmospheric CH_4 because such areas are unlikely to host well-established communities of methanotrophic bacteria capable of responding rapidly to short-term increases in soil moisture.

2.5 Results and Discussion

The following sections critically evaluate MeMo estimates, comparing the regional distribution of CH_4 uptake by MeMo and other published model predictions, as well as its main drivers in the context of available field data.

2.5.1 The global CH_4 uptake by soils

The average annual soil sink for atmospheric CH_4 estimated by MeMo is 33.5 ± 0.6 Tg CH_4 y^{-1} for the period 1990 to 2009 and it is greater than global uptake predicted using the P96 and C07 models (20 ± 3 Tg CH_4 y^{-1} and 29.3 ± 0.6 Tg CH_4 y^{-1}, respectively). The R99 model predicts a global sink of 38.1 ± 1.1 Tg CH_4 y^{-1}, which compares more favorably with the MeMo estimate. The observed differences in mean global soil uptake of atmospheric CH_4 estimated using models R99, C07 and MeMo forced with identical data are attributed primarily to three factors: (i) their respective mathematical solutions of reaction-transport equations (section 2.2), (ii) differences in parameterization of k_0 (section 2.3.3), and (iii) differences in formulation of r_N (section 2.3.6). The R99 model predicts soil uptake that is 12% and 24% greater, respectively, than fluxes estimated using MeMo and the C07 model. These differences are due to the R99 model applying a k_0 that is one order of magnitude greater than k_0 values used in the C07 model and MeMo. The amplifying effect of the large k_0 is partially offset by the semi-numerical approximation (Eq. 12) employed in the R99 model, which results in the final global CH_4 uptake flux being of similar magnitude to the MeMo and the C07 model estimates. Finally, the low uptake predicted by the C07 model is a consequence of the parameterization of the nitrogen inhibition effect ($r_{N,}$) and its direct modification of the CH_4 flux rather than the CH_4 oxidation activity (k_d) (section 2.3.3). Nitrogen inhibition was responsible for a global reduction in CH_4 uptake of 1.4 Tg y^{-1} in MeMo compared to 7.3 and 2.3 Tg y^{-1} in the C07 and R99 models, respectively.

2.5.2 Latitudinal distribution of CH_4 Uptake by Soils

The latitudinal distribution of soil uptake rates of atmospheric CH_4 predicted using the R99 and C07 models, and MeMo are shown in Fig. 2.5 accompanied by direct measurements of CH_4 oxidation rates from Dutaur & Verchot (2007) and a 10° running average. We chose to validate MeMo and previous models against regionally averaged observations to conduct the comparison at scales resolved by global models such as MeMo. This model is not intended to

represent fine-scale site-specific attributes of soil but rather broad regional soil characteristics and CH_4 uptake fluxes.

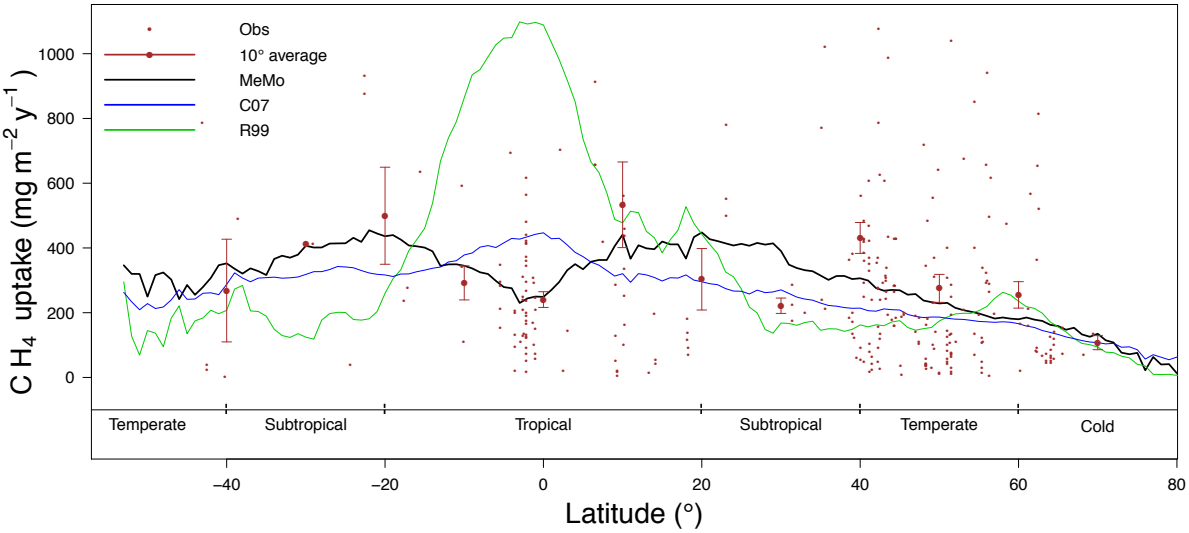

Figure 2.5 Latitudinal distribution of the soil uptake predicted by models R99 (green line), C07 (blue line) and MeMo (black line). Measurements of CH_4 uptake (small brown dots; Dutaur and Verchot, 2007) and a 10º running mean of direct observations (large brown dots for average with bars representing one standard deviation error).

The latitudinal distribution of observations reveals a scarcity of direct measurements of soil methanotrophy from sites in the southern hemisphere. Additionally, the frequency of measurements generally is low and rarely encompasses a full twelve-month period, which creates challenges for verifying model estimates of annual CH_4 uptake fluxes. Observations at specific latitudes typically exhibit a wide range of values, which are reflected in the large standard error bars calculated for the 10º running means (Fig. 2.5). Nevertheless, the averages of direct observations calculated for each 10° latitude interval show a distinct bimodal pattern with the lowest soil CH_4 uptake fluxes in the tropics and at high latitudes. Maximum rates of CH_4 uptake occur between 10 to 20° latitude in both hemispheres (Fig. 2.5). MeMo simulates a similar bimodal latitudinal distribution of CH_4 uptake fluxes with an RSME that is 16.8 mg CH_4 m^{-2} y^{-1} lower than other models when fitted to 10° latitudinal averages of observational data. In contrast, the C07 and R99 models both predict a latitudinal distribution of soil methanotrophy that has CH_4 uptake maxima in equatorial regions and lower rates of CH_4 oxidation at mid-latitudes (~40°N and 20 to 40° S), resulting in higher RSMEs of 28.6 and 72.1 mg CH_4 m^{-2} y^{-1}, respectively, when fitted to the 10° latitude averaged data. The R99 model significantly overestimates CH_4 uptake fluxes in the tropics (20°N to 20°S) and underestimates CH_4 oxidation in the subtropics (20 to 40° N and S), resulting in large differences for these

regions relative to the MeMo simulations (Fig. 2.6e). The C07 model predicts a latitudinal pattern of simulated CH_4 fluxes that is similar to R99; however, with much lower uptake fluxes in the tropics and no pronounced minima in the subtropics. Consequently, the RSME of the fit to observational data is much lower and regional differences relative to MeMo generally are smaller, ranging from 30% in the tropics to 20% in the subtropics (Fig. 2.6d).

2.5.3 Regional CH_4 Uptake by Soils

The regional differences between MeMo and the R99 and C07 models result from differences in the parameterization of factors that govern CH_4 oxidation rates in the models: k_0, $r_{SM.}$, r_T and r_N. The lower k_0 assigned to tropical wet forest (see section 2.3.2) accounts for the reduction in CH_4 uptake by tropical soil in MeMo. The strong agreement between MeMo simulation results and CH_4 uptake measurements presented in Fig. 2.5 suggests that the empirically derived lower k_0 value more accurately reflects soil CH_4 oxidation rates in the tropics. However, we note the possibility that additional factors, or unexpected combinations of current factors, may influence rates of atmospheric CH_4 uptake in the tropics in ways that are not explicitly represented in the models.

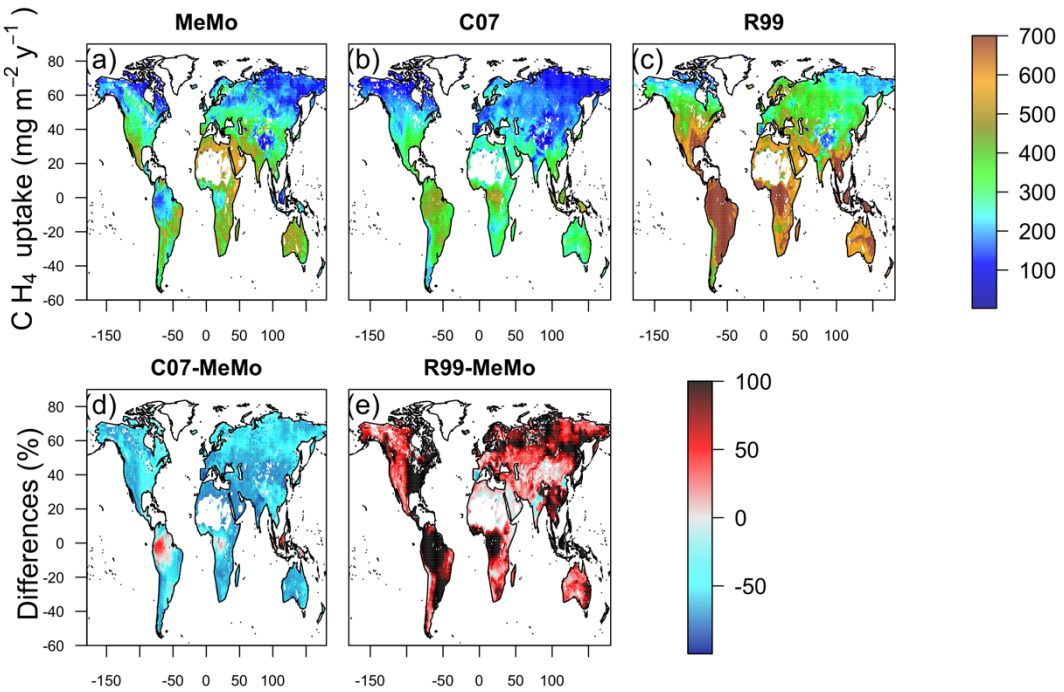

Figure 2.6. Annual mean CH_4 uptake by soil predicted using models (a) MeMo, (b) C07 and (c) R99 for the period 1990-2009. Differences between models expressed in percent are shown in panels (d) C07 minus MeMo and (e) R99 minus MeMo.

The influence of different environmental factors on soil CH_4 uptake was assessed by calculating the global CH_4 uptake flux while varying each factor (temperature, soil moisture and nitrogen input) independently and keeping other factors constant (Figs. 2.7, 2.8 and 2.9). Comparison of r_{SM} values reveals large differences across models in tropical wet regions (Fig. 2.7), which explains the contrasting predictions of CH_4 uptake by MeMo (213 mg CH_4 m^{-2} y^{-1}) versus models R99 (689 mg CH_4 m^{-2} y^{-1}) and C07 (329 mg CH_4 m^{-2} y^{-1}). Formulation of r_{SM} in MeMo (section 2.3.4) accounts for limitation of methanotrophic oxidation rates when soil moisture levels are >20% water content, a feature that is absent in the R99 and C07 models. In addition, the R99 model implements a linear decrease of r_{SM} for soil moisture conditions <20%, which results in a 60 to 80% reduction in CH_4 oxidation rates in the subtopics. The absence of this condition in models MeMo and C07 explains the significant differences in CH_4 uptake fluxes in subtropical regions (Figs. 2.5 and 2.6).

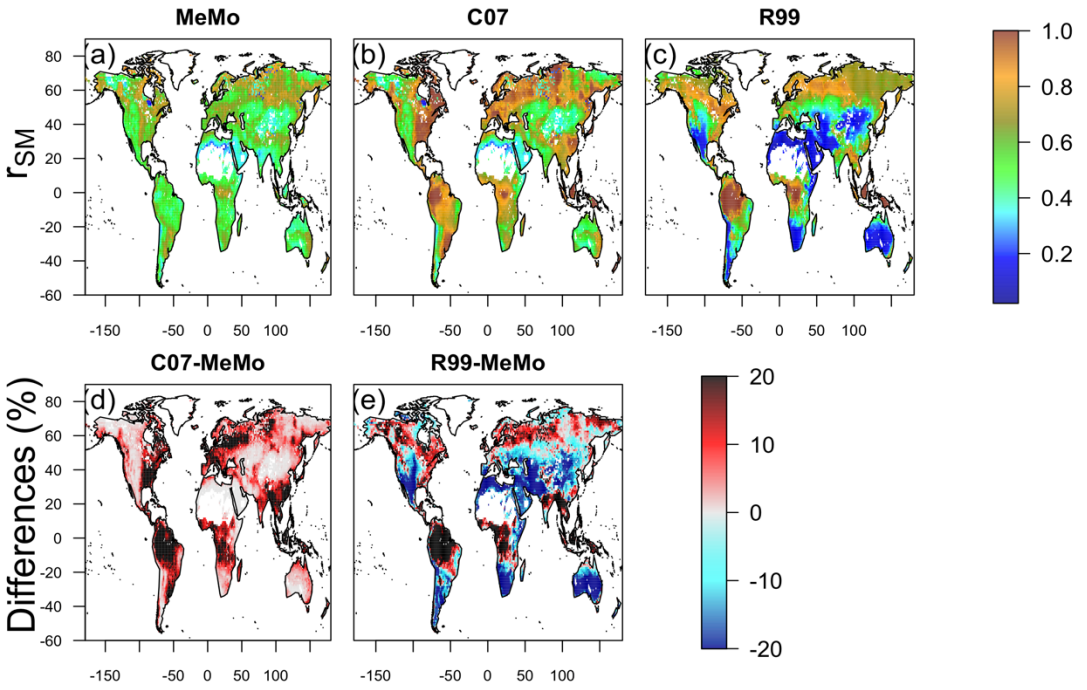

Figure 2.7. Soil moisture response (r_{SM}) of CH_4 oxidation simulated by models (a) MeMo, (b) C07 and (c) R99. Differences in model response expressed in percent are shown in panels (d) C07 minus MeMo, and (e) R99 minus MeMo.

Formulations of r_T are similar in the three models (section 2.3.4) and consequently, gridded maps of simulated r_T values exhibit broadly similar global patterns in which high r_T values are present at warm low latitudes and low r_T values are predicted at cold high latitudes. Notably, MeMo generally simulates r_T values that are approximately 20% lower than those predicted by the C07 and R99 models (Fig. 2.8) because of the revised formulation of the Q_{10}

value. MeMo and the C07 model simulate higher r_T values than R99 at high latitudes because of differences in parameterization of r_T at temperatures near 0°C.

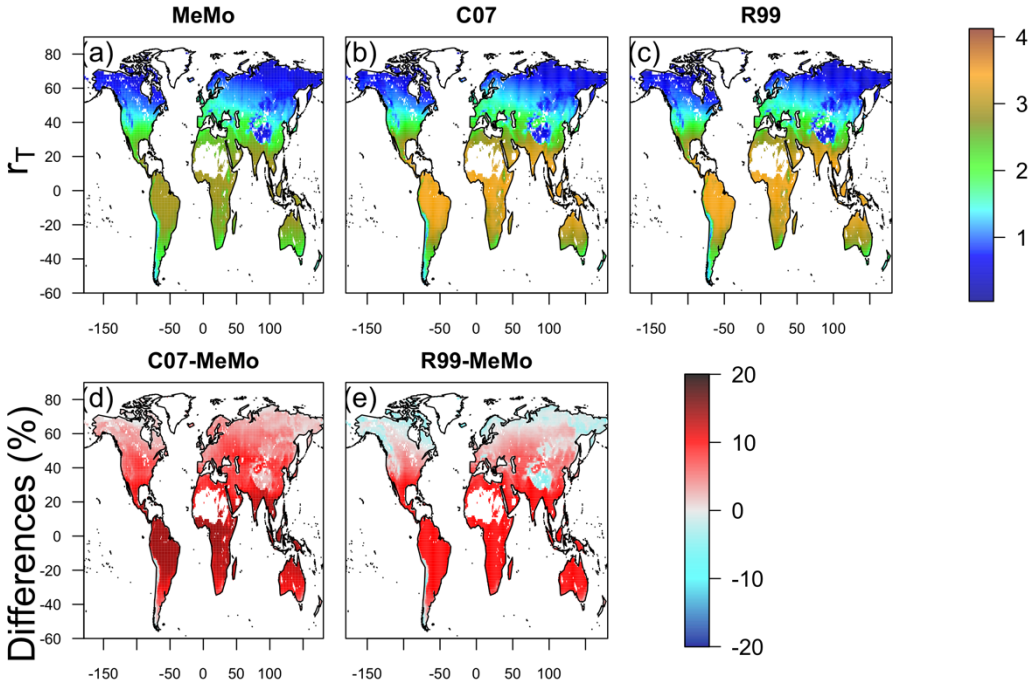

Figure 2.8 Temperature response (r_T) of soil methanotrophy simulated by models (a) MeMo, (b) C07, and (c) R99. Differences in model response expressed in percent are shown in panels (d) C07 minus MeMo, and (e) R99 minus MeMo.

Inhibition of soil methanotrophy due to N (r_N) differs significantly between the three models. Nitrogen inhibition of CH_4 oxidation rates is lower in MeMo compared to the R99 and C07 models, in particular, at mid-latitudes (Fig. 2.9). The R99 and C07 models formulate r_N as a function of agricultural intensity in contrast to MeMo, which uses modelled N deposition and N input via fertilizers. The difference in approach results in an r_N factor that is up to 20% higher in MeMo across most regions with the exception of high latitude areas (Fig. 2.9).

In regions of intense agricultural activity and high N deposition (~150 kg N ha^{-1}), such as Europe, the mid-western USA, China and India MeMo predicts a reduction in CH_4 uptake rates of up to 60% on average, which is consistent with R99 and C07 models. However, inhibition of methanotrophy simulated by MeMo in areas experiencing low rates of N deposition is much smaller than R99 or C07. The key limitation of the N effect approach adopted in the R99 and C07 models is the generalization of N inhibitory effects across different agricultural areas, crops and types of land management, which results in a homogeneous and excessive attenuation of CH_4 oxidation rates. In contrast, the MeMo r_N parameterization

employs a more conservative r_N factor and a realistic regional distribution, which is based upon observational data that is consistent with recent studies reporting that high rates of N deposition (10 kg N ha^{-1} y^{-1}) can reduce soil uptake of atmospheric CH_4 by ~8.6% (Fang et al., 2014; Zhang et al., 2008). Direct application of fertilizers at more extreme rates >300 kg N ha^{-1} y^{-1} can entirely eliminate uptake of atmospheric CH_4 by agricultural soil (Veldkamp et al., 2001). Nevertheless, the importance of accurate characterization of the attenuating effects of N addition on soil methanotrophy highlights the need for additional efforts to verify and refine parameterization of this key factor.

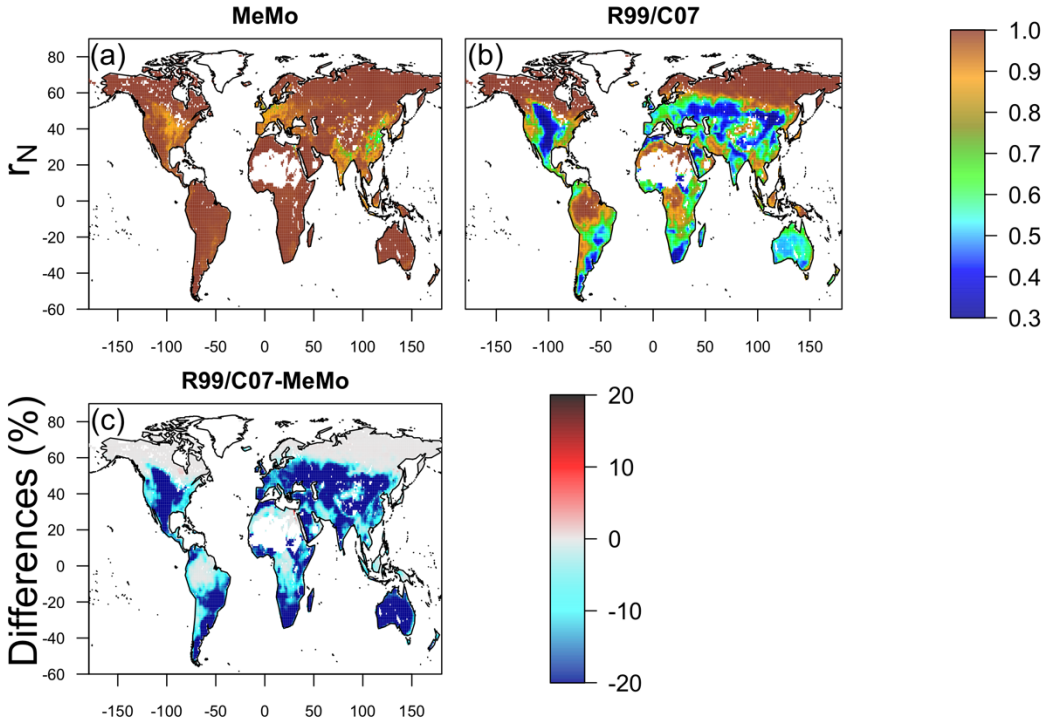

Figure 2.9 Response of soil methanotrophy to nitrogen effect (r_N) simulated by models (a) MeMo, (b) R99, and C07. The responses for models R99 and C07 are both shown in panel (b) because they have the same formulation. The difference in model response between models R99/C07 minus MeMo expressed in percent is shown in panel (c).

2.5.4 Model Limitations and Scope of Applicability

Several aspects of MeMo can be developed further, pending availability of new field data to improve estimation of global soil uptake of atmospheric CH_4. Firstly, the base oxidation rate of bacterial methanotrophy at 0°C (k_0) is a critical parameter necessary for accurate estimation of CH_4 uptake rates. There is presently a general dearth of published k_0 values for soil methanotrophy and moreover, ecosystem coverage is incomplete. Additionally, our parameterization for k_d accounts for methanotrophic activity in a one-dimensional soil matrix;

however, other studies have separated CH_4 uptake in soil from methanotrophy in the rhizosphere to improve estimates of total CH_4 uptake (*e.g.*, Sabrekov et al., 2016). This refinement has been modeled for local conditions but insufficient data about rhizosphere CH_4 oxidation rates prevent inclusion in MeMo and extension to a global scale. Secondly, the Q_{10} response of soil methanotrophy has been determined to date in only a small subset of ecosystems in which soils function as a sink for atmospheric CH_4. The majority of Q_{10} values have been determined for bacterial oxidation of CH_4 under laboratory conditions and there is considerable variability in values across different ecosystems. It should be noted that temperature varies with soil depth, a factor not considered in our model due to availability of data (temperature at the surface is used as a proxy of soil temperature) and scale limitations (our estimations are performed on a 1x1º grid, thus the variation in temperature with depth is not reflected in the global average). Thirdly, additional field observations of CH_4 uptake by soil are needed, in particular, long-term measurements at individual sites that capture seasonality and inter-annual variability and from regions that presently have minimal or no representation (*i.e.*, the southern hemisphere, semi-arid ecosystems, etc.) in the current pool of observations. Fourthly, additional observations and characterization of the effects of N deposition on soil methanotrophy are needed. The measurements ideally should be conducted *in situ* using N input rates that are appropriate for different environments and land use practices. MeMo can be used to guide new field and laboratory experiments to address the lack of parameterization data, in particular, k_0 and Q_{10} values for soil methanotrophy in different ecosystem and latitudes, and long-term *in situ* studies of N inhibition on CH_4 uptake by soil. It also can be used to compare results from short- and long-term investigations of CH_4 uptake in field and laboratory experiments.

MeMo is also parameterized to accommodate input of CH_4 from below (*i.e.*, subsurface methanogenesis or upward migration of deeply sourced CH_4); however, rigorous validation of that aspect of the model will require additional field observations, including better characterization of conditions under which CH_4 is produced in finely textured soils and deep sub-horizons. The presence, or periodic input, of high concentrations of CH_4 (*e.g.*, from permafrost melting) may impact competition for oxygen and niche space between low affinity CH_4-oxidizing bacteria and the high affinity methanotrophs responsible for uptake of atmospheric CH_4. Refinement and validation of the capacity for MeMo to account for upward migrating or autochthonous CH_4 will enable the model to be used to estimate CH_4 flux from intermittently wet environments, which may currently fall outside the scope of process-based wetland models.

The process-based nature of MeMo and the breadth of conditions for which it has been validated provide scope for using the model to quantify CH_4 uptake in soil in a broad range of scenarios. For example, MeMo could be used to determine global uptake of CH_4 by soil in the past during glacial or former interglacial periods. It may also be used to assess potential uptake rates of atmospheric CH_4 in future climate scenarios and further elevated tropospheric CH_4 mixing ratios. Additionally, MeMo can be used to evaluate the impact of different proposed policies and mitigation strategies for managing the atmospheric burden and growth rate of CH_4 because of its capacity to evaluate different future scenarios based upon parameterization of key drivers that impact rates of CH_4 uptake by soil globally.

2.6 Conclusions

A novel processed-based model was developed to simulate uptake of atmospheric CH_4 by soil, which was refined using newly reported experimental data and the introduction of recent insights into physical and biological mechanisms that drive soil methanotrophy. The general analytical solution proposed by Ridgwell et al. (1999) and Curry (2007) was modified to account for a maximum depth of CH_4 uptake and to quantify upward migration and consumption of CH_4 produced *in situ*. Representation of the effects of N deposition and input via fertilizers, soil moisture and temperature on methanotrophy were improved based upon newly available data and recent advances in characterization of these processes. Finally, the utilization of a different base oxidation rate k_0 for methanotrophy in different regions was proposed because its value changes in relation to environmental conditions.

MeMo simulations produced a closer fit to observational data than two previous soil methanotrophy models (Ridgwell et al., 1999; Curry 2007). MeMo and observational data show a similar bi-modal latitudinal distribution of atmospheric CH_4 uptake by soil with the lowest fluxes at the equator and high-latitudes, and largest uptake fluxes at mid-latitudes. Previous models simulated a dissimilar pattern with large uptake fluxes in equatorial regions, a difference that results primarily from improved representation of the soil moisture effect in MeMo.

MeMo simulations indicate that global soil uptake of atmospheric CH_4 is reduced 4% on average and by as much as 60% in regions that receive high rates of atmospheric N deposition and N input from fertilizers. Globally, N deposition and input via fertilizers attenuates the soil sink for atmospheric CH_4 by 1.38 Tg yr^{-1}, which is two to five times less

than previously reported values because of the refined representation of the nitrogen inhibition on soil CH_4 oxidation in MeMo.

The accuracy of quantifying the modern soil sink for atmospheric CH_4 is improved using MeMo. In addition, the model can be used to explore changes in the relative importance of soil methanotrophy in the global CH_4 cycle in the past and the capacity of the soil sink to consume atmospheric CH_4 under future global change scenarios.

2.7 Code and Data Availability

MeMo was implemented in the free open source computing environment and programming language R (version 3.0.1). The model code and the model output for 1990-2009 are available as a supplement to Murguia-Flores et al. (2018) together with a post-processed driving dataset to run an example model case study for the year 2000 and a Read Me file.

CHAPTER 3

Present-day spatial and temporal dynamics of global CH_4 uptake by soils

Contributions and acknowledgements

This chapter is adapted from a research article published in *Geoscientific Model Development* (Murguia-Flores et al., 2018). All co-authors (S. Arndt, A. L. Ganesan, G. Murray-Tortarolo and E. R.C. Hornibrook) provided assistance with editing and advised on aspects of this work. Three anonymous referees gave insightful comments on previous versions of the published manuscript. All work presented in this chapter is my own.

Murguia-Flores, F., Arndt, S., Ganesan, A. L., Murray-Tortarolo, G., & Hornibrook, E. R.C. (2018). Soil Methanotrophy Model (MeMo v1. 0): a process-based model to quantify global uptake of atmospheric methane by soil. *Geoscientific Model Development*, *11*(6), 2009.

3.1 Introduction

There is large interannual variability and uncertainty in the accounting of global CH_4 budget, particularly for processes that consume CH_4 (Kirschke et al., 2013). Soil methanotrophy is the only biological sink for CH_4 and its rate is highly dependent on environmental conditions. The total global soil sink is similar in size to global emissions of CH_4 from rice paddies (Kirschke et al., 2013) and consequently year-to-year changes in factors that impact rates of soil CH_4 oxidation may contribute to variability in the interannual growth rate of atmospheric CH_4.

The global soil sink has been estimated using different approaches, it has been estimate removes approximately 28 to 39 Tg of CH_4 y^{-1} from the atmosphere (Dörr et al., 1993; Potter et al., 1996; Hein et al., 1997; Ridgwell et al., 1999; Smith et al., 2000; Dutaur & Verchot 2007; Curry, 2007; Spahni et al., 2011; Zhuang et al., 2013 and Murguia-Flores et al., 2018). Previous estimates of CH_4 uptake by soils were based on global, mechanistic model simulations, atmospheric inversions and the upscaling of field observations- although the latter is compromise by the limited availability of direct observational data, particularly across arid ecosystems and southern latitudes

Atmospheric CH_4 uptake by soils varies through multiple spatial and temporal scales. Interannual variability is small, likely due to a compensatory effect between changes in moisture and temperature at a global scale. As some places get wetter other get drier and the water effect cancels, creating a balancing effect on the global annual CH_4 uptake. Similar patterns have been observed in the global land CO_2 sink changes (Jung et al., 2017) Latitudinally, the CH_4 consumption by soils is larger over the tropics were warm and dry conditions prevail and the region between 45º N-45º S is responsible for 80% of the global uptake (Zhuang et al., 2013). Seasonally, the uptake is larger during July and lower during February, following the active bacterial season of the northern hemisphere (Zhuang et al., 2013). Finally, the uptake seems to change accordingly with the changes in atmospheric CH_4 concentration and major climate fluctuations (*i.e.* ENSO), as shown by Curry (2007) for the period 1979 to 1999 and by Zhuang et al. (2013) for the last century (1900-2000).

The global soil consumption also varies with ecosystem types due to differences in the ecosystem´s physical components: temperature, precipitation, and land use change. For example, seasonal temperature variations control the uptake across temperate forest (Morishita et al., 2004), tundra (Lau et al., 2015) and boreal forest (Whalen et al., 1992), leading to higher rates during the summer compared to the winter. In the tropical deciduous forest, tropical wet forest, short-grass steppe, boreal forest and tundra soil moisture exerts a dominant role, with the highest uptake rates registered during the dry season (Singh et al., 1997; Mosier et al, 2002; O´Conell et a., 2018; Luo, et al., 2013; Borken et al., 2006; Lau et al., 2015; Blankinship et al., 2010). Land use change also controls the uptake, mostly via a negative effect on soil CH_4 consumption. For example, in several comparisons between agricultural regions and natural ecosystems, the first show a reduction between 10 to 62% in the uptake rates due to the N additions via fertilizers (Dobbie et al., 1996; Mossier et al., 1997; Pawlson et al., 1997). On a similar note, the natural ecosystems that received N inputs via atmospheric deposition also reported a reduced oxidation rates (Steudler et al., 1989; Zhang et al., 2008; Morishita et al., 2011).

Several global models have considered the CH_4 uptake response to the variations on the climate to estimate the spatial and temporal variations in the global CH_4 uptake by soils. For example, Potter et al. (1996) ran a global diffusion model and estimated that steppe is the ecosystem with the highest uptake rates, and savanna the largest CH_4 sink. Other global models such as those built by Ridgwell et al. (1999) and Curry (1997) estimate the tropical wet forest as the ecosystem with the highest uptake rate and the largest proportion of the total global uptake. The previous discrepancy shows the inherit differences across the model construction

and assumptions and points out to a need to review their result in the light of new data availability and new observed data to compare them with. Thus, it is clear that the global CH_4 uptake by the soils needs to be revised and recalculated to simulate the spatial and temporal dynamics with novel models, that employ state of the art forcing data and the most recent direct measurements used to improve their parameterization (as seen in chapter 2).

Based on the previous, the aim of this chapter is to provide a new quantitative and modelling approach of the global atmospheric CH_4 uptake by soils as well as an assessment of global and regional soil uptake variability across ecosystem types and seasons, using the novel developed process-based model MeMo (Murguia-Flores et al., 2018).

3.2 Methods

The process-based Methanotrophy Model (MeMo) (Murguia-Flores et al., 2018), a novel model to quantify atmospheric CH_4 uptake by soils was used. The new analytical solution and revisited physical relationships proposed in MeMo are useful for the estimation of atmospheric CH_4 uptake by soils in the full profile and consist on two parts: 1) the CH_4 diffusion into the soil is controlled by the physical soil properties, soil moisture and temperature, and 2) the microbial CH_4 oxidation, is calculated based on a constant base oxidation rate (for an uncultivated and moist soil at 0°C) is modified by temperature, soil moisture and nitrogen inputs (via fertilizers and deposition). The full description of the model is available in Murguia-Flores et al. (2018) (Chapter 2).

For the results showed in this chapter, MeMo was forced with the same driving data described in chapter 2 at a 1x1º resolution.

3.3 Results and Discussion

3.3.1 Global CH_4 Uptake by Soils

MeMo predicts an average annual global flux of 33.5 ± 0.6 Tg CH_4 y^{-1} for the period 1990 to 2009. Uncertainty in this flux was calculated as the standard deviation of annual global CH_4 uptake. The estimated global uptake compares well with estimates from terrestrial ecosystem models, DGVMs and global atmospheric inversions (Table 3.1). Zhuang et al. (2013) determined a similar average global uptake flux of 34 ± 2 Tg CH_4 y^{-1} during the 21st century using a process-based model included in the Terrestrial Ecosystem Model (TEM) while Spahni et al. (2011) estimated an uptake flux of 38.9 Tg CH_4 y^{-1} using the LPJ-WHyMe DGVM. Hein

et al. (1997) predicted a similar flux through atmospheric inversions but with a greater level of uncertainty (30 ± 15 Tg CH_4 y^{-1}). Upscaling of field measurements of soil methanotrophy rates from 120 different studies spanning a wide range of ecosystems yielded an uptake flux of 36 ± 23 Tg CH_4 y^{-1} (Dutaur & Verchot, 2007). The large uncertainty associated with the mean flux results from differences in data representation for ecosystems and a tendency for sampling to be conducted seasonally rather than annually. In contrast, flux estimates based upon extrapolation of long-term records of CH_4 uptake in a smaller number of soil types resulted in an estimated flux of 28.7 Tg CH_4 y^{-1} (Dörr et al. 1993). Similarly, global extrapolation of measurements made solely on northern European soils yielded a sink strength of 29 Tg CH_4 y^{-1} (Smith et al. 2000).

Table 3.1 Global CH_4 uptake estimations

Methodology	Reference	Global uptake by soils (Tg CH_4 y^{-1})
Observation	Dörr et al. (1993)	28.7
Observation	Smith et al. (2000)	29
Observation	Dutaur & Verchot (2007)	36 ± 23
Atmospheric inversions	Hein et al. (1997)	30 ± 15
Model (P96)	Potter et al. (1996)	20 ± 3
Model (R99)	Ridgwell et al. (1999)	38.1 ± 1.1
Model	Spahni et al. (2011)	38.9
Model (C07)	Curry (2007)	29.3 ± 0.6
Model	Zhuang et al. (2013)	34 ± 2
Model (MeMo)	**(This study)**	**33.5 ± 0.6**

3.3.2 Temporal and Spatial Variability of Soil CH_4 Uptake

Field observations of soil uptake of atmospheric CH_4 are generally sparse both spatially and temporally. Consequently, our quantitative understanding of CH_4 uptake fluxes across different ecosystems and seasons is limited. Models provide a means to quantitatively explore spatial and temporal patterns of soil methanotrophy on scales that cannot be readily captured by field-based observations. Therefore, once tested and validated (see Chapter 2), MeMo was used to quantitatively assess the variability of soil CH_4 uptake in different climate zones and ecosystems on seasonal time scales.

3.3.3 Regional Variability

The relative contribution of soil in each climatic zone to global uptake of atmospheric CH_4 as predicted by MeMo is summarized in Table 3.2. Soil in the northern hemisphere is estimated to account for approximately two thirds (65%) of the total global sink for atmospheric CH_4

because of the uneven distribution of landmasses between the northern and southern hemispheres. Notably, terrestrial areas in the northern subtropical and temperate zones collectively account for ~45% of the global soil sink for atmospheric CH_4. The southern tropical zone contributes a further ~19% to soil uptake of CH_4. The southern subtropical and northern tropical zones are estimated to contribute almost equally (~14%) to total CH_4 uptake (Table 3.2). The smallest proportion of soil CH_4 oxidation occurs in the southern temperate (0.6%) and northern polar (5%) zones due to a combination of small land area and low rates of CH_4 uptake. Model predictions of CH_4 uptake by climatic zone provides insights into the relative importance of each region in the global CH_4 cycle but additionally begins to facilitate analysis of potential responses of the soil CH_4 sink within each zone to global change both due to climate and land management.

Table 3.2 MeMo CH_4 uptake estimates by region.

Regions	Regional gridded mean (mg CH_4 m^{-2} y^{-1})	Total land area (10^{12} m^{-2})	Total CH_4 uptake (Tg CH_4 y^{-1})	% of total
Cold zone (60°-90° N)	100.1	18.7	1.87	5.6
Temperate zone (40°-60° N)	217.0	31.0	6.7	20.0
Subtropic zone (20°-40° N)	326.6	26.4	8.6	25.7
Tropical zone (0°- 20° N)	309.2	15.1	4.6	13.9
Northern Hemisphere Total:		**91.2**	**21.9**	**65.3**
Temperate zone (40°-60° S)	234	1.1	0.2	0.6
Subtropic zone (20°-40° S)	363.7	13.3	4.8	14.3
Tropical zone (0°- 20° S)	313.9	20.8	6.5	19.4
Southern Hemisphere Total:		**35.2**	**11.6**	**34.6**

Further analysis of soil CH_4 uptake by ecosystem types (Table 3.3) shows that the highest gridded mean rates of CH_4 oxidation are associated with tropical deciduous forests (602 mg CH_4 m^{-2} y^{-1}). The relatively low soil moisture content during the dry season (Appendix B, Figure B1.3) and the consistently high mean annual temperature (Appendix B, Figure B1.7) in such ecosystems promote high rates of soil methanotrophy. Furthermore, the soil typically possesses a low clay content (Appendix B, Figure B1.2), which results in higher porosity that enhances gas diffusion and promotes higher rates of CH_4 oxidation. In comparison, rates of CH_4 uptake by soil in open and dense shrubland, temperate evergreen forest and savanna ecosystems (Table 3.3) are ~100 mg CH_4 m^{-2} y^{-1} lower but still highly significant globally.

Dense and open shrubland are characterized by constant climatic conditions (temperate and relatively low soil moisture; Appendix B Figures B1.7 and B1.3, respectively) throughout the year, which in combination with a soil texture that typically is sandy results in high annual CH_4 uptake rates (Tate et al., 2007). In contrast, high annual rates of CH_4 uptake in temperate evergreen forests result from elevated rates of soil methanotrophy during summer months, indicating that temperature is a key driver of CH_4 oxidation in such ecosystems (Borken et al., 2006; Ueyama et al., 2015; Wang & Ineson, 2003). Savannas share many climatic conditions with tropical deciduous forests but also commonly experience wildfire during the dry season. Both ecosystem types though are characterized by a marked seasonality driven by the presence or absence of precipitation in combination with a consistent high mean annual temperature (Appendix B, Figure B1.7 and B1.3), which collectively support high rates of CH_4 uptake by soil.

Tundra, taiga, polar desert and other ecosystem types that are common at high latitudes (Appendix B, Figure B1.10) are characterized by the lowest mean annual rates of soil methanotrophy (<180 mg CH_4 m^{-2} y^{-1}) because of low temperatures throughout most of the year. MeMo also predicts low rates of CH_4 uptake in tropical humid forest (332 mg CH_4 m^{-2} y^{-1}) due to low rates of bacterial CH_4 oxidation and the negative impact of high soil moisture levels on gas diffusion (see Chapter 2). The CH_4 uptake rates estimated by MeMo are consistent with field observations by Dasselar et al. (1998) and Luo et al. (2013), which indicate that excess soil moisture strongly attenuates CH_4 uptake rates across a range of ecosystem types.

Finally, the global significance of each ecosystem type as a CH_4 sink depends strongly on spatial extent as well as CH_4 oxidation rates. Open shrubland (19.7%), grassland and steppe (15.0%), and savanna (13.4%) are the most important ecosystem types contributing to the global CH_4 soil sink (~48% collectively; Table 3.3) in MeMo because of high mean rates of CH_4 uptake (392 to 518 mg CH_4 m^{-2} y^{-1}) in combination with a large areal extent globally (14 x 10^{12} to 23 x 10^{12} m^2). This finding is similar to the estimate reported by Potter et al. (1996) that warm and relatively dry ecosystems, such as semi-arid steppe, tropical savanna, tropical seasonal forest, and chaparral, account for 40% of soil uptake of atmospheric CH_4 globally. Moreover, Luo et al. (2013) reported the highest annual CH_4 uptake rates in dry savanna as part of a long-term field investigation of soil methanotrophy in several ecosystem types. Singh et al. (1997) also observed CH_4 uptake rates that were higher in savannah than temperate forest. Although both model simulations and available field observations suggest these ecosystems

are important global sinks for atmospheric CH_4 there is presently a dearth of field measurements for warm and dry environments relative to temperate ecosystems.

Table 3.2 MeMo CH_4 uptake estimates by ecosystem type from Ramankutty & Foley (1999) land cover classification.

Ecosystem type	Global gridded mean (mg CH_4 m^{-2} y^{-1})	Total land area (x10^{12} m^{-2})	Total CH_4 uptake (Tg CH_4 y^{-1})	% of total
Tropical Deciduous Forest	602 ± 63	4.2	1.6	4.7
Open Shrubland	518 ± 134	23.3	6.6	19.7
Temperate Broadleaf Evergreen Forest	512 ± 82	2.0	0.6	1.7
Savanna	500 ± 132	14.1	4.5	13.4
Dense Shrubland	481 ± 90	6.1	2.4	7.1
Grassland/Steppe	392 ± 110	15.8	5.0	15.0
Temperate Needleleaf Evergreen Forest	347 ± 90	3.9	1.2	3.5
Temperate Deciduous Forest	321 ± 70	5.2	1.4	4.1
Tropical Evergreen Forest	332 ± 45	12.5	2.5	7.4
Boreal Deciduous Forest	282 ±117	5.7	1.5	4.4
Boreal Evergreen Forest	269 ± 94	9.1	2.4	7.1
Mixed Forest	182 ± 82	13.4	2.7	8.0
Tundra	176 ± 143	6.2	1.1	3.2
Polar Desert/Rock/Ice	105 ± 48	0.4	0.01	0.0
Total		**124.1**	**33.5**	**100**

3.3.4 Seasonal Variability

Global annual uptake of atmospheric CH_4 by soil exhibits a marked seasonality that reflects the dominance of the northern hemisphere in the soil sink. The highest simulated CH_4 uptake fluxes occur during June, July, August (JJA) (10.3 Tg CH_4) followed by September, October and November (SON) (10.1 Tg CH_4), March, April and May (MAM) (6.8 Tg CH_4), and finally, December, January and February (DJF) (6.3 Tg CH_4) (Fig. 3.1).

Methane uptake in the cold and temperate regions of the northern hemisphere generally is characterized by the largest seasonality, exhibiting an amplitude of 30 mg CH_4 m^{-2} mo^{-1}. In these regions, modeled uptake of CH_4 by soil is controlled strongly by temperature and consequently, ecosystems common at these latitudes (*e.g.,* boreal, needle leaf, temperate deciduous, mixed forest, polar deserts/rock/ice and tundra) show pronounced seasonal trends (Fig. 3.2), which also are evident in field measurements (*e.g.*, Priemé & Christensen, 1997) and emphasized in local mechanistic models (*e.g.*, Oh et al., 2016). These finding suggest that the soil CH_4 sink in such ecosystems may be more sensitive to future change as a result of global warming.

In contrast, soil methanotrophy in temperate regions in the southern hemisphere are characterized by a weaker seasonality having an amplitude of 17 mg CH_4 m^{-2} mo^{-1} due to the prevalence of grassland and steppe, which contrasts with a dominance of forest in the northern hemisphere. Seasonality of soil CH_4 uptake fluxes is even more muted in tropical and subtropical environments (<10 mg CH_4 m^{-2} mo^{-1}) because of favorable and stable environmental conditions. Tropical deciduous forest and tropical evergreen forest, which are common in these climate zones are characterized by relatively constant CH_4 uptake fluxes throughout the year (Fig. 3.2); however, MeMo predicts greater seasonality (20 mg CH_4 m^{-2} mo^{-1}) of CH_4 uptake by soil in drier subtropical ecosystems, such as open shrubland, savanna and grasslands (Fig. 3.2) because of seasonality in soil moisture.

Notably, northern temperate forest in summer (JJA) was the ecosystem and time period possessing the highest average monthly CH_4 uptake fluxes (76.7 mg CH_4 m^{-2} mo^{-1}) simulated by MeMo. During the rest of the year, the largest soil sink for atmospheric CH_4 occurred in the southern hemisphere in tropical deciduous forest of central Africa (DJF, 69.5 mg CH_4 m^{-2} mo^{-1}; MAM, 73.5 mgCH_4 m^{-2} mo^{-1}; SON, 75.5 mg CH_4 m^{-2} mo^{-1}). This finding is significant because field observations of soil methanotrophy in northern temperate forest during summer are the measurements most commonly extrapolated to an annual basis, which may lead to a possible overestimation of global CH_4 uptake fluxes.

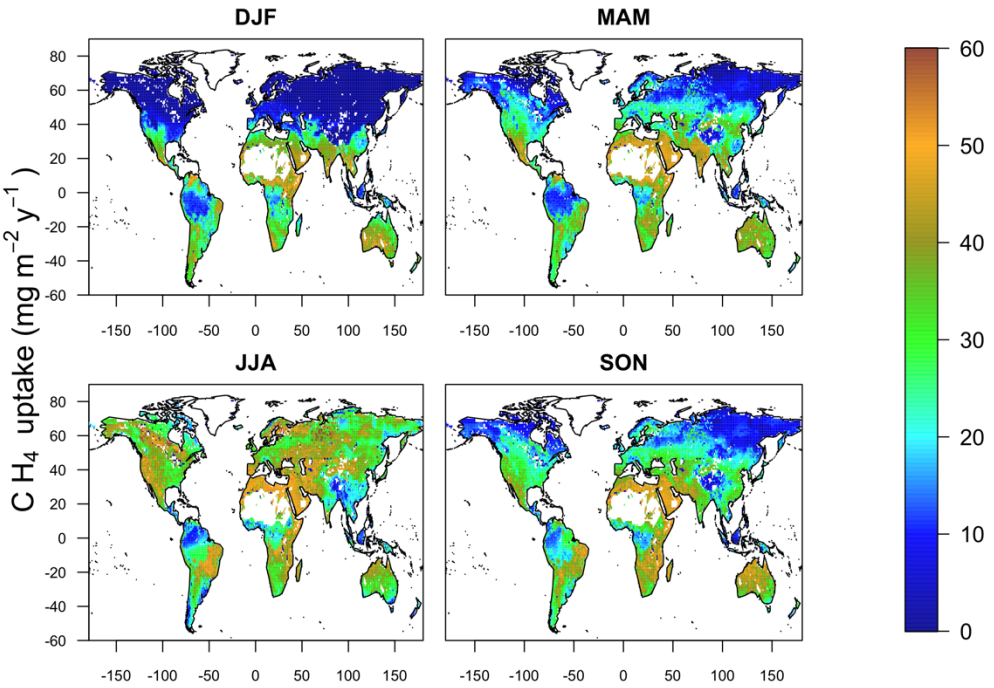

Figure 3.1 Seasonal uptake of atmospheric CH_4 by global soils predicted by MeMo for the period 1990 to 2009.

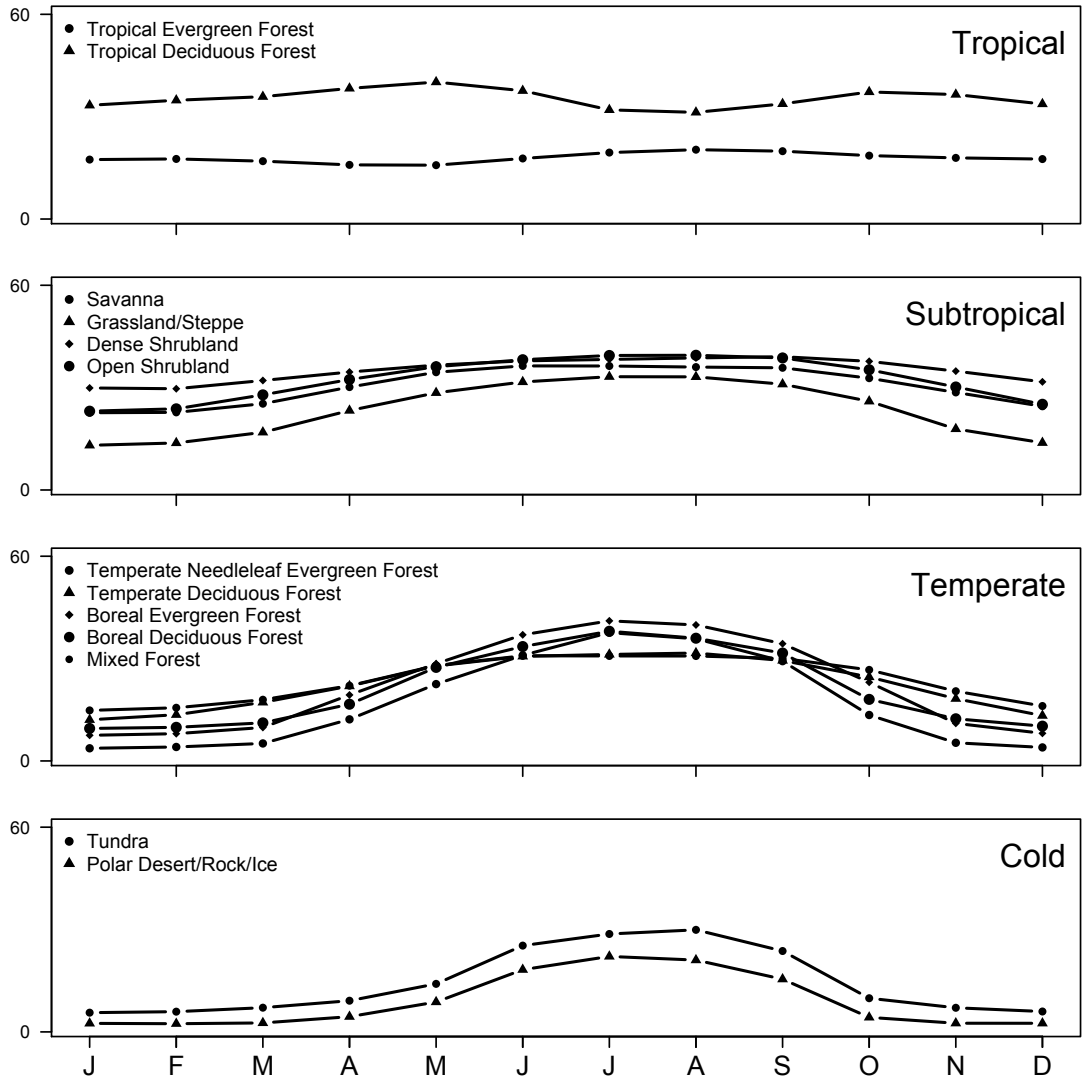

Figure 3.2 Seasonal patterns of soil uptake of atmospheric CH_4 by ecosystem for the four regions: cold, temperate, tropical and subtropical using MeMo model for the period 1990-2009.

3.4 Conclusions

MeMo simulations supported by observational data indicate that warm and semiarid regions are the most efficient soil sink for atmospheric CH_4. In these regions, tropical deciduous forest and dense open shrubland are characterized by relatively low soil moisture and constant temperature during the year, which are key factors that promote high rates of CH_4 uptake by soil. In contrast, cold regions possessed the lowest CH_4 uptake rates, in particular, tundra and boreal forest, which have a marked seasonality driven by temperature, making soil methanotrophy in such areas potentially sensitive to future global climate change. The warm and wet tropical evergreen forest biome has CH_4 uptake rates that are ~50% less than warm and semiarid regions because excess soil moisture impacts soil-atmosphere gas exchange,

resulting in a smaller k_0 (1.6 x10^{-5} s^{-1}) (see chapter 2). The extensive area of shrubland, grassland, steppe and savanna globally yield a high total uptake of CH_4; however, there is presently a dearth of experimental data for these biomes and additional field observations are required to strengthen validation of MeMo simulations for these globally extensive areas.

CHAPTER 4.

Global dynamics of atmospheric CH_4 uptake by soil for the last century and future RCP´s

Contributions and acknowledgements
This chapter is adapted from a research article to be submitted in 2018 to *Global Change Biology*, for publication. A. L. Ganesan, S. Arndt, and E. R.C. Hornibrook provided assistance with editing and advised on aspects of this work. All work presented in this chapter is my own.

4.1 Introduction

Global CH_4 uptake by soils has been increasing to the point where it has doubled during the last century from ~10 at preindustrial era to 24-36 Tg CH_4 y^{-1} at the end of 1990,s (Curry, 2009; Zhuang et al., 2013), however the drivers and the mechanism of this change are still poorly understood, offering little insight into any potential future changes. It has been suggested that anthropogenic activity has and will increase the relative significance of the CH_4 soil sink in the global CH_4 budget. Previous work reported a potential increase in the soil CH_4 uptake between 23% (Curry, 2009) to 280%, relative similar than the current emissions by ruminants (Zhuang et al., 2013) by 2100, depending on the emission path and the model which is employed to estimate the uptake.

The rate of methanotrophy in soil is controlled by several environmental factors including temperature, soil texture, moisture and nitrogen (N) content (Czepiel et al., 1995; Le Mer & Roger, 2001; Wang et al., 2005). The influence of these factors on rates of CH_4 oxidation has been widely studied both at the ecosystem level and under laboratory conditions. Positive correlations have been consistently reported between temperature and rates of CH_4 oxidation in soil (Castro et al., 1995; Butterbach-Bahl & Papen, 2002; Rosenkranz et al., 2006; Luo et al., 2013). Atypically low and high soil moisture levels both have a negative impact on rates of atmospheric CH_4 consumption. A soil moisture content of ~20% appears to yield optimum rates of CH_4 uptake in different ecosystems, including tropical forests, short grass steppe and tundra (Adamsen & King, 1993; Mosier, 2002; Burke et al., 1999; Castro et al., 1995; Epstein et al., 1998; Klemedtsson & Klemedtsson, 1997; McLain & Ahmann, 2007; West et al., 1999). Soil texture impacts the ability of soil to retain water and influences diffusion of atmospheric CH_4 and O_2 into soil because of its control on pore size and

connectivity. Thus sandy soil generally exhibits higher rates of CH_4 uptake than silt-rich soil followed by clayey soil (Born et al., 1990; Dörr et al., 1993). The influence of N input from atmospheric deposition and fertilizer application is more complex; however, the majority of studies report inhibition of soil methanotrophy with increased addition of N (Aronson & Helliker, 2010; Bodelier & Laanbroek, 2004; Fang et al., 2014).

Human activities during the last century have altered the uptake of CH_4 in the soil via two mechanisms: the increase of greenhouse gases concentration in the atmosphere and by land use change. Compared to the pre-industrial era, atmospheric CH_4 concentrations have tripled (680-1800 ppb) (Etheridge et al., 1998; Saunois et al., 2016) and reactive nitrogen in soils has doubled primarily through chemical fertilizers (Nishina et al., 2017) and atmospheric deposition. We have also modified more than 40% of the ice-free land to grow crops and raise cattle (Foley et al., 2005). Additionally, during last century, anthropogenic emissions have resulted in a global temperature increase of ~0.8ºC (since 1880) (Hansen et al., 2010). All of these factors have changed the rate at which CH_4 is consumed in the soils globally.

It has been suggested that future changes in the size of the global CH_4 sink will be primarily driven by an increase in atmospheric CH_4, with other factors (soil moisture, nitrogen deposition and temperature) playing a smaller part (Curry, 2009; Zhuang et al., 2013). The positive effect of atmospheric CH_4 concentrations on methanotrophy has been demonstrated in laboratory experiments using different soils and increasing ambient CH_4 concentrations (Nesbit et al., 1992). Similarly, one of the first global model estimates of the soil CH_4 sink by Potter et al. (1996) is based on the assumption that the diffusion of CH_4 into the soil exerts the dominant control on CH_4 uptake by soils. However, several long-term field and laboratory experiments that investigate the effects of other drivers of soil methanotrophy (Castro et. al., 1995; Czepiel et al., 1995; Blankinship et al., 2010; Luo et al., 2013; Yu et al., 2017) show that other environmental factors, such as temperature and soil moisture exert the dominant control on CH_4 uptake at the ecosystem scale. Therefore, the main control of methanotrophy depends on the specific environmental and local conditions and recent global models resolve the effect of a plethora of environmental factors on CH_4 uptake (e.g. Ridgwell et al., 1999, Curry, 2007; Zhuang et al., 2013; Murguia-Flores et al., 2018).

In spite of the previous, at the global scale, a formal attribution of the drivers of soil methanotrophy is limited. Although previous studies have attempted to characterize global methanotrophy and its drivers from 1900 to 2100, (Curry, 2009 and Zhuang et al., 2013), using previous Special Report Emission Scenarios (SRES) to estimate future uptake values. They lack a spatial component, which is fundamental to bring in line regional field and laboratory

experiment results with global modelling. This is necessary to be able to comprehend the size of this sink in the context of the global CH_4 budget and assess how this may change in the future using the recent Representative Concentration Pathways (RCPs) (Taylor et al., 2012).

The recently developed process-based model MeMo v1.0 (Murguia Flores et al., 2018) is applied in this chapter and forced with: a) historical period divided in early (1900-1979) and late (1980-2015), and b) four future scenarios (2016-2100) to answer the following questions: 1) What is the impact of soil CH_4 uptake changes on the global CH_4 budget, in the last century and over future scenarios? (Section 3.2). 2) What are the main drivers of this change? (Section 3.3.1). 3)What are the process-level mechanisms controlling these drivers? (Section 3.3.2).

4.2 Methods

The process-based Methanotrophy Model (MeMo) (Murguia-Flores et al., 2018) estimates the CH_4 uptake in the full profile. The full description of the model is available in Murguia-Flores et al. (2018) (Chapter 2). A schematic description is provided below in Figure 4.1.

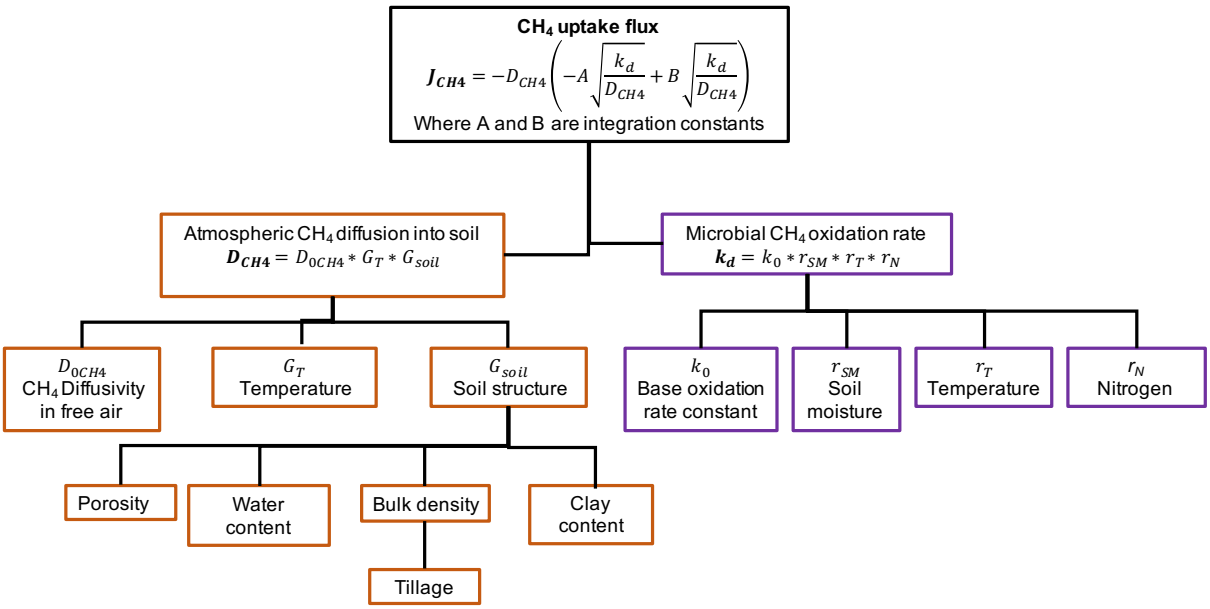

Figure 4.1 Methanotrophy Model (MeMo) consist on two parts: 1) the CH_4 diffusion into the soil (D_{CH4}), controlled by the physical soil properties, water content and temperature, and 2) the microbial CH_4 oxidation (k_d), based on a based oxidation rate (for an uncultivated and moist soil at 0°C), which is modified by temperature, soil moisture and nitrogen inputs (via fertilizers and deposition).

4.2.1 Model drivers

MeMo was run at a monthly and 1°x1° spatial resolution, for the historical period, which was divided into the early (1900-1979), and late (1980-2015) periods, and for the future, which was defined as 2016 to 2100. The boundary between the early and late historical periods occurs at the time of maximum rate of change in global CH_4 uptake by soils.

For the historical simulations (1900-2015), MeMo was forced using global monthly observations of soil moisture (SM) of top-layers (Dorigo et al., 2011; Sitch et al., 2015), temperature at the surface (CRU3.1 from Harris et al., 2014), atmospheric CH_4 concentration (Rigby et al., 2008), N deposition (Lamarque et al., 2013), N input from fertilizers (Nishina et al., 2017), soil bulk density and clay content (Shangguan et al., 2014). Table 4.1

For the future simulations (2016-2100), MeMo was forced by the four Representative Concentration Pathways (RCP) 2.6, 4.5, 6.0 and 8.5, driving data. SM, temperature and atmospheric CH_4 concentration were extracted from the mean of nine Earth System Models (ESM) (Table 4.1) For each RCP (Taylor, 2012). N deposition were taken from Lamarque et al., 2013 and N input via fertilizers, was assumed to change linearly with N deposition. Soil bulk density and clay content were considered the same as the historical period (Shangguan et al., 2014). Table 4.1

For this work, the effect of tillage was included in MeMo, its effect was contained as the positive response over bulk density, which is enhance by tillage in around 10%, according with Dam et al. (2005); Lapurlanes & Martinez (2001); Bauer & Blak (1981); Unger & Jones (1998); Osunbitan et al. (2005) and Grant & Landford (1993) (Figure 4.1). Thus, tillage was assumed to occur on cropland area, which was constrained on the basis of observed and modelled agricultural data from Chini et al. (2014), for both historical and future runs.

Table 4.1 Driving data and sources for the Historical and Future runs.

Drivers	Historical run (1900-2015)	Future run (2016-2100)
Temperature	CRU3.1 (Harris et al., 2014)	Mean of nine ESM: CCSM4, GFDL-ESM2G, HadGEM2, IPSL-CM5A-LR, PSL-CM5A-MR, MIROC-ESM, MIROC-ESM-CHEM, NorESM1-M and NorESM1-ME. (Taylor et al., 2012)
Soil moisture	CRU3.1 (Harris et al., 2014)	
Atmospheric CH_4 concentration	Rigby et al., 2008	

N deposition	Lamarque et al. (2013)	Lamarque et al. (2013)
N fertilizers	Nishina et al. (2017)	Increases linearly with N deposition
Bulk density and clay content	Shangguan et al. (2014)	Shangguan et al. (2014)
Tillage (agricultural area)	Chini et al. (2014)	Chini et al. (2014)

In all simulations, areas with less than 0.5% average annual SM content were masked (*e.g.*, Sahara Desert) because areas with low but episodic SM conditions lead to spurious model signals. The vegetation mask from Ramankutty & Foley (1999) was used to set the different microbial oxidation rates (k_0) associated with different ecosystems.

4.2.2 Data analysis

4.2.2.1 Contribution to global budget and Damköhler number

The global annual mean CH_4 uptake was calculated for each period (1900-1979; 1980-2015) and future RCP (2065-2100 for RCPs 2.6, 4.5, 6.0, 8.5) and the associated spatial distribution. To assess the potential of soil methanotrophy in offsetting CH_4 emissions, we calculated the percentage of uptake relative to total and anthropogenic CH_4 emissions, using the emissions values from Ciais et al. (2013).

The process of soil methanotrophy is different from the main sink for atmospheric CH_4, reaction with OH, in that it is controlled by both physical as well as biological factors (see chapter 2). On the one hand, the uptake flux depends on the diffusive transport of CH_4 across the soil-atmosphere interface, which is controlled by the apparent diffusion coefficient D_{CH4} (temperature, soil structure and water content), as well as the concentration gradient across the interface and, thus atmospheric CH_4. On the other hand, it is determined by the microbial oxidation of CH_4 in the soil, which is controlled by the rate constant for CH_4 oxidation, k_d (temperature, soil moisture and nitrogen) and the soil CH_4 concentration. The response of the uptake flux to changes in environmental conditions thus depends on the combined response of reaction and transport processes to these changes. For instance, the projected future increase in atmospheric CH_4 concentration will only translate into an increased CH_4 uptake if the resident microbial community can efficiently oxidize the additional amount of CH_4 and, thus maintain or even increase the concentration gradient across the soil-atmosphere interface.

With the objective to evaluate the relative importance of CH_4 microbial oxidation (k_d) and CH_4 diffusion (D_{CH4}) rates the Damköhler number were used. Those

numbers (Da) are a useful ratio for determining whether diffusion rates or reaction rates are more 'important' for defining a steady-state chemical distribution over the length of interest, L. Da values of one imply equal diffusion and reaction rates and the distance from this equilibrium allows one to establish the dominant process. Da numbers >1 imply faster CH_4 oxidation compared to CH_4 diffusion over the length scale L, resulting in steeper gradient shallower penetration depth and thus higher uptake fluxes. Da<1 imply an increased importance of diffusion rates over reaction rates, less step gradients and thus lower uptake fluxes. It has been widely used in ecology to contrast biological and physical effects of microbial mediated processes (Landsdown et al., 2015). It is a dimensionless number that relates the reaction to the transport rate over a length scale of interest:

$$\text{Da} = \frac{reaction\ rate}{transport\ rate} = \frac{kd * L^2}{D_{CH4}} \quad (2)$$

Where D_{CH4} and k_d are functions of temperature, soil structure and soil moisture and temperature, soil moisture and nitrogen, respectively (see Figure 4.1). L is the length scale of interest. Here L=25 cm was applied.

The length of interest L was calculated as the length where the reaction resembles an equilibrium between global average of k_d and D_{CH4}. The previous is due to the fact that if we used a complete L (>100cm) the calculation would be dominated by the diffusion and the changes in the equilibrium between both processes would not be visible. Figure 4.2 shows that a depth smaller than 10cm leads to small Da values, while a depth larger than 50cm leads to large Da values. Thus, we assumed the equilibrium to occur at 25cm of depth and tested the limits of global average k_d and D_{CH4} for the full soil profile. This is shown by the fact that across all high k_d simulations the reaction was always diffusion limited (Figure 4.2 dashed lines), while across all low k_d simulations the reaction was limited by the microbial activity (Figure 4.2 solid lines). In addition, when k_d-values are small (e.g. in frozen and moist regions) the uptake does not increase with the atmospheric CH_4 concentration and that bacterial activity can be a strong limitation for the flux.

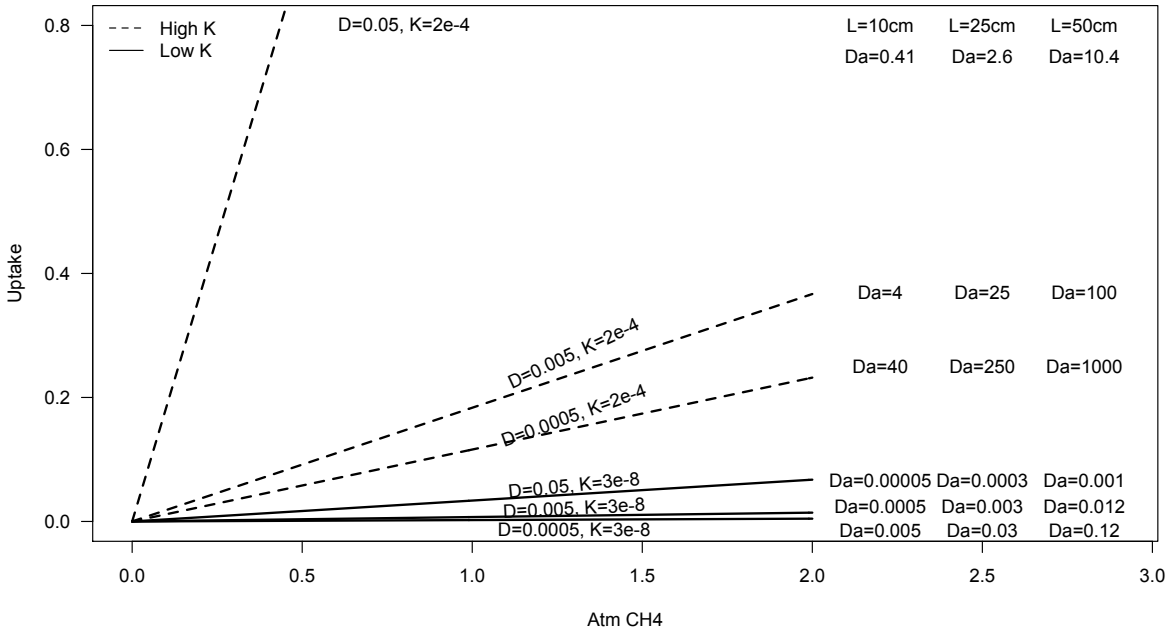

Figure 4.2. Damköhler numbers (Da) for different k_d (K) and D_{CH4} (D) values. Dashed lines represent high values of k_d (highest found on the model) and solid line represent low values of k_d (lowest found on the model). In addition, the Da numbers varied with the defined depth, the values of Da for the different k_d and D_{CH4} combinations are below the depth values: 10 cm, 25 cm and 50 cm.

4.2.2.2 Relative contribution of the drivers to CH_4 uptake by soils

We conducted a series of factorial experiments to determine the effect of each driver on the total change in global CH_4 uptake during the respective time periods. One parameter was allowed to vary over time while the remainder were set to monthly values of the year that started the period (*i.e.* 1900 for the historical period and 2016 for the future scenarios). We conducted 30 runs in total: all parameters varying, only temperature varying, only SM varying, only atmospheric CH_4 varying, only N varying and only tillage varying, for the five scenarios (historical + four RCPs).

The net change in CH_4 uptake over each time period was estimated by calculating the finite difference in the global uptake rate each year for each experiment and integrating over the period. This allowed us to quantify the contribution of each driver to the total trend (both globally and for each grid cell). The limitation of this approach is that any interactions between drivers would not be accounted for, however these are found to be small as the sum of the individual driver contributions is close to simulation using the full suite of time varying parameters.

The mechanisms behind each driver were analysed using the following methods. The degree to which atmospheric CH_4 concentrations affected CH_4 uptake was evaluated by analysing the linear correlation between atmospheric concentration and uptake. Temperature effects were explored by spatially evaluating the number of days that allowed for methanotrophic activity (*i.e.* when $r_T>0$, Fig 4.1) in the historical periods and in the RCPs. Soil methanotrophy has optimal uptake at 20% water content and thus, a change in SM can either increase or decrease soil uptake. We thus categorized spatial changes into four categories: positive changes in both SM and uptake, negative changes in both SM and uptake, positive changes in SM and negative changes in uptake, and negative changes in SM and positive changes in uptake. To explore the N effect on the global uptake change, we calculated the change in the cropland area between the historical period and the RCPs.

4.3 Results and Discussion

4.3.1 Global CH_4 uptake by soils: past, present and future

Fig. 4.3 illustrates the evolution of global CH_4 uptake for all simulated scenarios over the period between 1900-2100. Model results show that CH_4 uptake by global soils increased considerably over the early historical period from 17.3 Tg y^{-1} in 1900 to 30.6 Tg y^{-1} in 1979 with a growth in CH_4 uptake of 0.16 Tg y^{-2}. During the late historical period, global CH_4 uptake increased at a rate of 0.14 Tg y^{-2} to a global mean uptake of 35.7 Tg y^{-1} in 2015. In addition, global uptake estimates obtained by forcing the model with observational climatic data for the period between 1900-2018 were similar to those forced with ESM output (Fig. 4.3). Model results are consistent with other published estimates. Zhuang et al. (2013) estimated an increase in global soil uptake during the 20th century from 18 Tg y^{-1} to 32 Tg y^{-1} by applying a process- based model forced with TEM (Terrestrial Ecosystem Model) input and observational climatic data (CRU) (Mitchell and Jones, 2005). In addition, top-down and bottom-up models have estimated a mean of 30 Tg CH_4 y^{-1} (min 28 and max 33 Tg y^{-1}) of uptake, for the decade 2000-2009 (Bergamaschi et al., 2009; Bousquet et al., 2011; Fraser et al., 2013; Beck et al., 2012).

The uptake across future scenario runs reveals diverging patterns. In the most extreme RCP8.5, CH_4 uptake continuously increases from 34.1 Tg y^{-1} in 2016 to a maximum uptake of 82.7 Tg y^{-1} (or increases by 41%) by year 2100, while in RCP2.6 it continuously decreases to a minimum uptake of 25.7 Tg y^{-1} (or decreased 24%) in 2100. The rate of change between 2016 and 2100 is 0.5 and -0.09 Tg y^{-2}, respectively. Intermediate scenarios RCPs 4.5 and 6.0, are

characterized by an increase CH_4 uptake until mid- century to a peak of 38.1 and 41.6 Tg y^{-1} (years 2052 and 2080, respectively) and a subsequent decrease to stabilize at values similar to the 2016 uptake rates (33.8 and 35.6 Tg y^{-1} respectively). Thus, for these intermediate scenarios, the overall net rate of change is minimal (-0.01 and -0.006 Tg y^{-2} respectively) (Figure 4.4).

Our results for future scenarios are consistent with other published estimates. Curry (2009) used a process- based model forced with Special Report on Emissions Scenarios (SRES) A1B (Nakicenovic et al., 2000), data and estimated uptake of 30.4 Tg y^{-1} in 2100. This estimate lies at the lower end of our estimates because his model has proved to underestimate the uptake flux due to the mathematical model structure (Murguia-Flores et al., 2018) as SRES A1B is one of the highest emissions scenario. Zhuang et al. (2013) also forced a process-based model with the previous IPCC SRES A1FI, A2, B2 and B1 (Nakicenovic et al., 2000). They estimated 45–140 Tg CH_4 y^{-1} at the end of 2090s or an increase of 20% in SRES B1 and 280% in SRES A1F1. Soil uptake in the most extreme scenario A1F1 is similar to our results in RCP8.5.

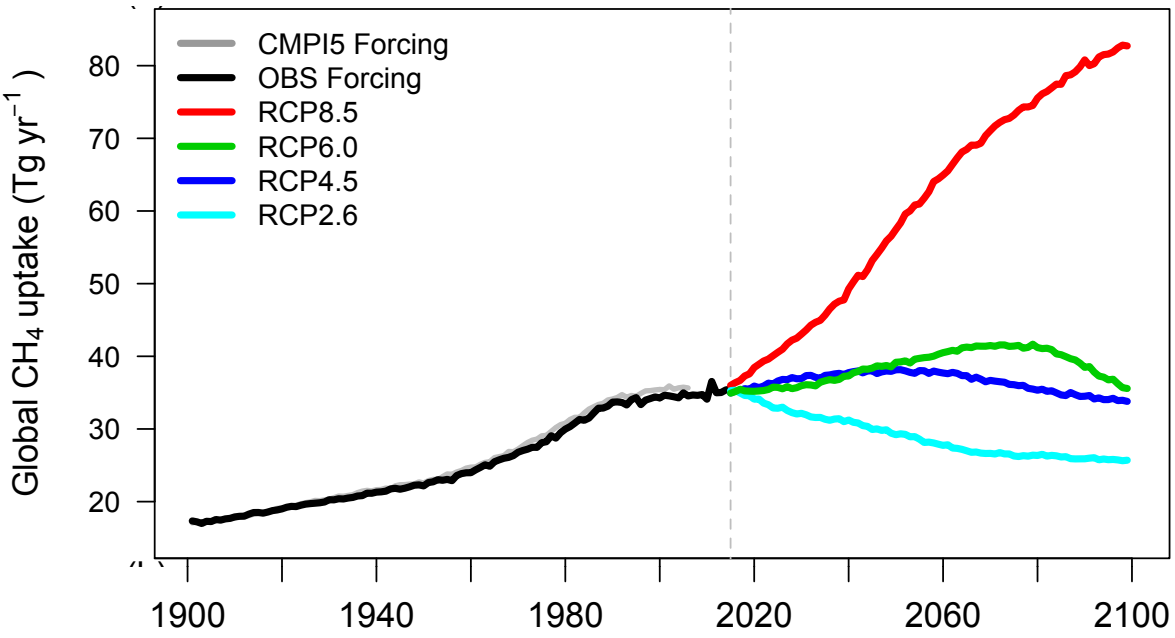

Figure 4.3 Changes in the rate of CH_4 uptake by soil from 1900 to 2100. Soil CH_4 uptake from 1900 to 2015 shows model results forced with observed driving data (black) and with CMIP5 modeled data (grey) values. Soil methanotrophy rates from 2015 to 2100 are modelled based upon the four RCPs (2.6, 4.5, 6.0 and 8.5).

Figure 4.4 illustrates the regional patterns of mean uptake fluxes for each scenario, as well as difference plots between the future scenarios (2069-2100) and the late historical period

(1980-2015). The simulations for RCP2.6 reveals a decrease in CH_4 uptake for all regions, while uptake increases for all regions in RCP8.5. Regional uptake patterns are more complex in the intermediate scenarios RCPs 4.5 and 6.0. Although model results for RCPs 4.5 and 6.0 predict a global uptake at the end of the century that is close to present-day soil uptake, important regional differences and, in particular, opposing regional trends can be observed (Fig. 4.4). Both scenarios show an increase in uptake over high latitudes and wet regions in South America and a decrease in central and south Africa, central Australia and east Asia.

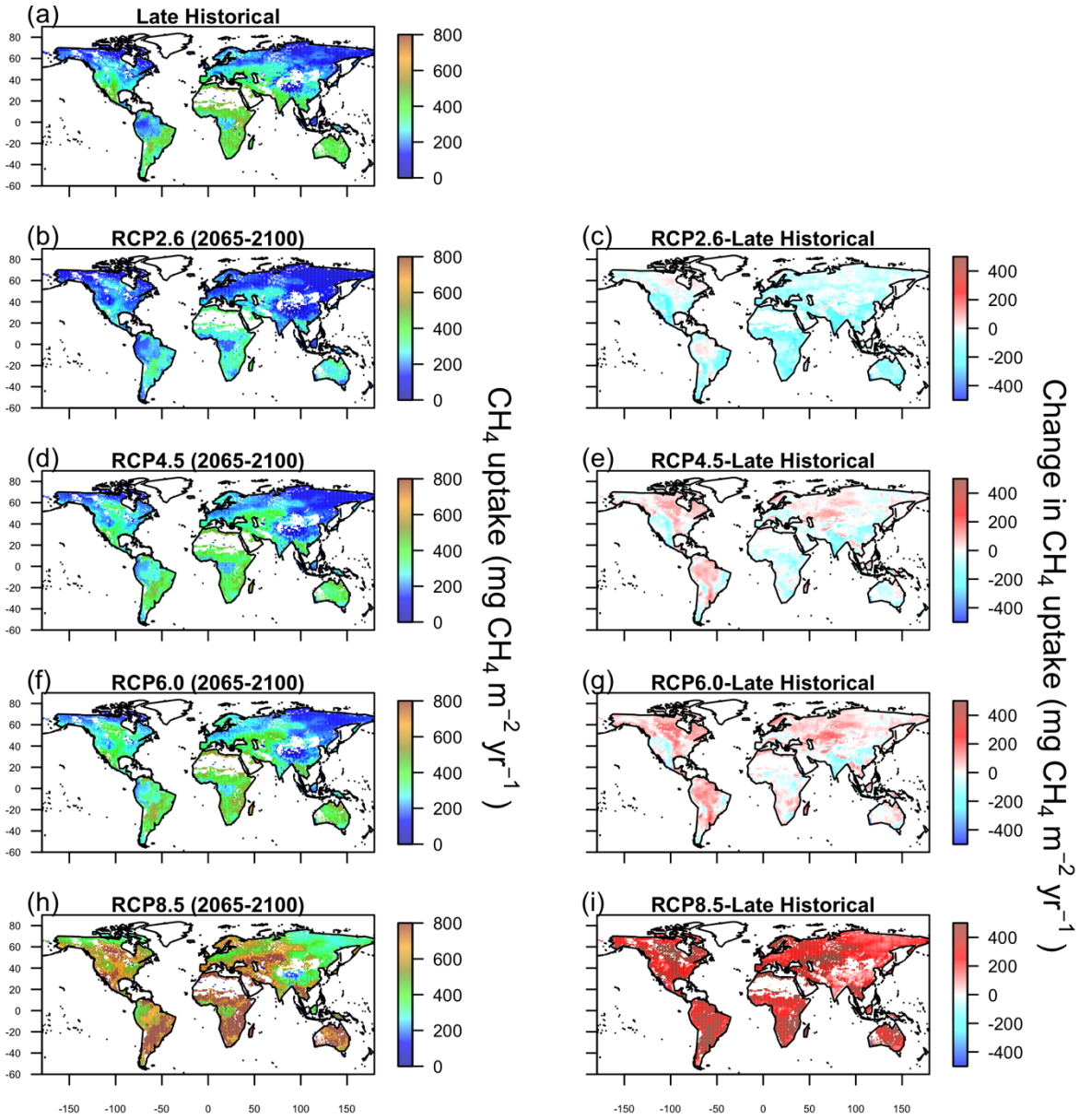

Figure 4.4 Gridded mean soil CH_4 uptake rate for (a) late historical (1980-2015) and late 21st century (2065-2100) in (b) RCP2.6, (d) RCP4.5, (f) RCP6.0 and (h) RCP8.5. The differences in soil uptake of atmospheric CH_4 between the late historical period and each RCP scenario are shown in panels (c), (e), (g) and (i).

4.3.2 Changes in the contribution of soil methanotrophy to the global CH_4 budget

Our results show that the global soil CH_4 sink represents 4.8% of the total CH_4 emissions over the early historical period (1900-1979). This fraction increased to 6.1% during the period between 1980 and 2015. Across the RCP scenarios, the global soil CH_4 sink represents 7% of total emissions on average (Table 4.2).

The fraction of the anthropogenic CH_4 emission consumed by the soils increases substantially in the future. The fraction was 8.0% in the early historical and 10.3% in the late historical period and could potentially be as high as 18% in RCP2.6 (Table 4.2). This suggests that soils could potentially consume a larger proportion of the anthropogenic CH_4 emissions in future RCPs and become a more important sink to stabilize atmospheric CH_4 concentrations. Collins et al. (2018) show that mitigation of CH_4 emissions is a key driver to stabilizing global temperature rise to 1.5-2.0 ºC at the end of 2100.

Table 4.2 Total CH_4 and anthropogenic CH_4 emissions, and soil uptake of CH_4 during the early and late historical periods, and the four RCP scenarios during the late 21st century. Values presented are the means over the periods with one standard deviation variability.

Period	Total CH_4 emissions	Anthropogenic CH_4 emissions	Soil Uptake (Tg yr^{-1})	% CH_4 uptake of total emissions	% CH_4 uptake of anthropogenic emissions
1900-1979	470 ± 104	280 ± 54	22.2 ± 3.6	4.8±0.7	8.0±1.2
1980-2015	550 ± 68	330 ± 60	34.0 ± 1.5	6.1±0.2	10.3±0.4
2065-2100 RCP2.6	366 ± 33	145 ± 18	26.1 ± 0.4	7.1±0.1	18.0±0.2
2065-2100 RCP4.5	480 ± 47	230 ± 37	35.1 ± 0.9	7.3	15.2
2065-2100 RCP6.0	542 ± 62	270 ± 41	39.9 ± 2.1	7.3	14.7
2065-2100 RCP8.5	1273 ± 143	935 ± 115	84.4 ± 3.8	6.6	9.0

Previously published results have shown that the uptake has and will likely increase in response to changes in multiple environmental factors that control both CH_4 transport and microbial consumption in the soil (Singh, 2010). For the historical period, both early and late there was a clear geographical pattern: in cold and wet regions transport rates dominate over reaction rates (Da<1), while in hot and dry regions reaction rates become more important relative to transport rates (Da>1). In the first case, low microbial reaction rate constant (k_d) are cause by low temperatures, high moisture or a combination of both. As a result, microbial CH_4

oxidation is less efficient, resulting in low concentration gradients and, thus lower fluxes. In hot and dry regions, the favorable environmental conditions result in an efficient bacterial CH_4 oxidation and, thus steeper concentration gradients. As a consequence, the soil's efficiency to respond to increasing atmospheric CH_4 concentrations increases. However, although uptake fluxes generally increase, they also reveal a higher sensitivity to diffusion coefficients D_{CH4} (see Figure 4.3). Hence, regions that are characterized by high k_d and Da closer to 1 (hence a balanced importance of reaction and transport rates) will show the strongest response to increasing atmospheric CH_4 concentrations.

For instance, the tropical region of the South America has two major climatic zones, each with different controls for the soil uptake: the tropical wet forest and the tropical dry forest. The wet region is controlled by the microbial reaction (Da<1) due to optimum temperatures for methanotrophs, while the high soil moisture limits the gas diffusivity through the soil. On the opposite, the dry region is controlled by the diffusion (Da>1), in spite of the high temperatures that lead to high reactions rates, mostly because the low soil moisture leads to high diffusion rates that overpass the microbe capability to oxidize it (Figure 4.5, a,b,c).

Over the future RCPs 2.6, 4.5 and 6.0, the global increase in temperature results in a general increase in reaction rate constants k_d, leading to generally higher uptake fluxes, but also an increased sensitivity of uptake fluxes to diffusion rate constants. Particularly across the NH, an increase in Damköhler numbers from Da<1 to Da>1 indicates the increased importance of reaction rates. Across those regions, environmental conditions, in particular temperatures become more favorable for microbial oxidation resulting in an increased potential of the soil to respond to increasing atmospheric CH_4 concentrations.

The previous implies that the effects of changing temperature, SM and N can alter the CH_4 oxidation by soils, altering its biological component and the flux, particularly in regions where microbial reaction is going to control the flux (cold and wet areas). As a result, these drivers could partially decouple the soil sink dependency from the global atmospheric CH_4, resulting in higher consumption rates than expected simply by the increase in transport processes.

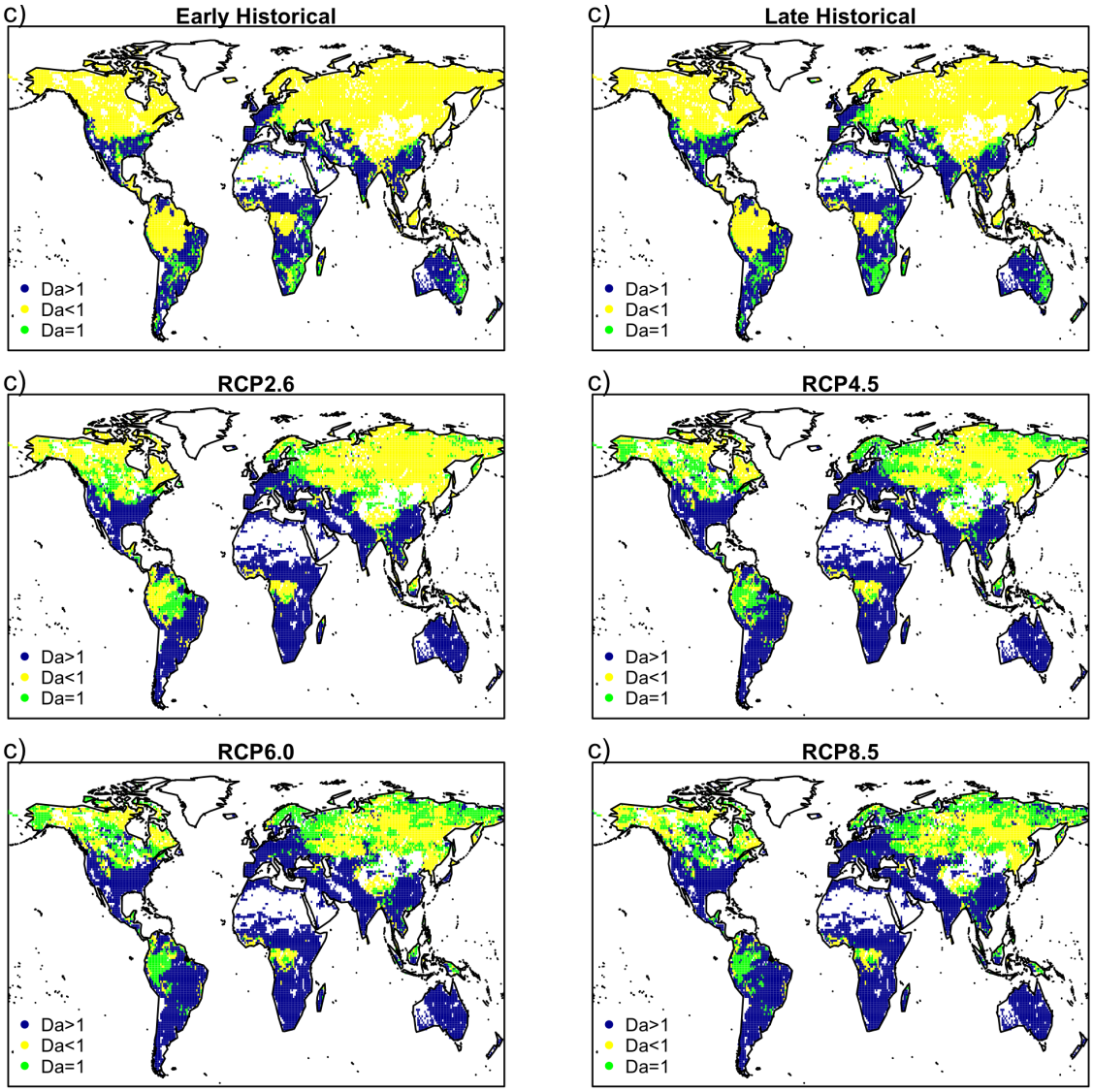

Figure 4.5 The spatial distribution of physical and biological processes controlling soil uptake of atmospheric CH_4 during (a) 1900 to 1979, (b) 1980 to 2015, (c) RCP2.6, (d) RCP4.5, (e) RCP6.0, and (f) RCP8.5, all of them for the period 2065-2100. Damköhler (Da) numbers are used to characterize areas where the physical diffusion rate of atmospheric CH_4 into soil controls the soil sink (Da < 1) or microbial reaction rate dominates CH_4 uptake (Da > 1), or both processes are in relative equilibrium (Da=1).

4.3.3 Drivers of change: Global Trends

To understand the drivers of the global soil CH_4 uptake, we quantified the contribution of each driver to simulated changes in the global soil CH_4 sink. Figure 4.6 shows the total uptake change and the contribution of each driver (atmospheric CH_4, temperature, SM and N).

The CH_4 uptake rate increased by 13.2 Tg y^{-1} from 1900 to 1979 and by 5.0 Tg y^{-1} from 1980 to 2015. Model results show that most of this increase was driven by an increase in atmospheric CH_4 concentration, supported by the capacity of the microbial community to

respond to increasing fluxes. However, in the last three decades of the century (1980-2015) through to the future, other factors start playing an important role in driving the trend. This is most evident in areas where environmental factors currently limit microbial oxidation rates, for example over high latitudes (due to low temperature and high SM). The increase in temperature explained only 10% of the change during 1900-1970 but 18% of the change between 1980-2015 and could potentially drive as much as 34% of the change in uptake in RCP6.0. Additionally, during the early historical period, N inputs to the Earth system inhibited the methanotrophy by 0.8 Tg yr^{-1} (7%), however it is likely that the effect will persist in future RCPs inhibiting between 0.6 and 0.9 Tg yr^{-1} (9-13 %) (Figures 4.6 and 4.7).

The future change in the size of the global soil sink strongly depends on the RCP scenario. A decrease of -11.2 Tg y^{-1} and -1.0 Tg y^{-1} was simulated for RCP2.6 and in RCP4.5, respectively, from 2016-2100. Similar to the early and late historical periods and in line with previous suggestions, the decrease in the soil CH_4 sink in RCP2.6 is mainly driven by the decrease in atmospheric CH_4 concentrations, which accounts for -12.0 of -11.2 Tg y^{-1} of the uptake variation. The opposing effects of increasing temperature (10%), SM changes (0%) and N changes (5%) play a minor role. The small net decrease in CH_4 uptake simulated for RCP4.5 by 2100 is driven by a balance between the negative effect of decreasing atmospheric CH_4 concentrations, which explain half of the total trend -4.6 of -1.0 Tg y^{-1} and the positive effects of temperature and N, which accounted for 2.4 and 1.1 Tg y^{-1} (Figure 4.6).

An increase in the size of the global CH_4 sink of 6.0 and 57.0 Tg y^{-1} was simulated for RCPs 6.0 and 8.5 respectively (Figure 4.6) from 2016 to 2100. Similar to the early and late historical scenarios and RCP2.6, the maximum increase in global CH_4 uptake simulated for RCP8.5 is mainly driven by changes in atmospheric CH_4 concentrations, explaining 80% (45.7 of 57 Tg y^{-1}) of the change. The increase in global temperature accounts for the remainder of change (7%). While atmospheric CH_4 concentration changes still represent an important driver in RCP6.0 (explaining 34% of the change or 2.0 of 6.0 Tg y^{-1}), temperature became the dominant driver controlling the majority (70% or 4.3 of 6.0 Tg y^{-1}) of the change. In general, tillage had a small effect over the uptake in all scenarios/time periods (less than 1%) and will therefore not be discussed further.

Atmospheric CH_4 concentration is the main driver of the global annual trends (increasing or decreasing) across all time periods, except for RCP6.0. This is likely the result of the dominant effect of CH_4 diffusion to the process, which leads to a linear relationship between the two components of the cycle (atmosphere and soils) (r=0.84). Other studies have found similar results, where uptake increases with CH_4 concentration, for example, Nesbit &

Breitenbeck (1992) in cultivated soils and Lau et al., (2015) in Artic mineral soils. Whalen & Reeburgh, (1990) observed increased methanotrophy activity even at unrealistically high CH_4 concentration (500 ppm). The previous also explains the trends in RCPs 4.6 and 6.0, where atmospheric CH_4 stabilizes by the end of the century. As a result, atmospheric CH_4 has a smaller total control over the trends in comparison to other factors.

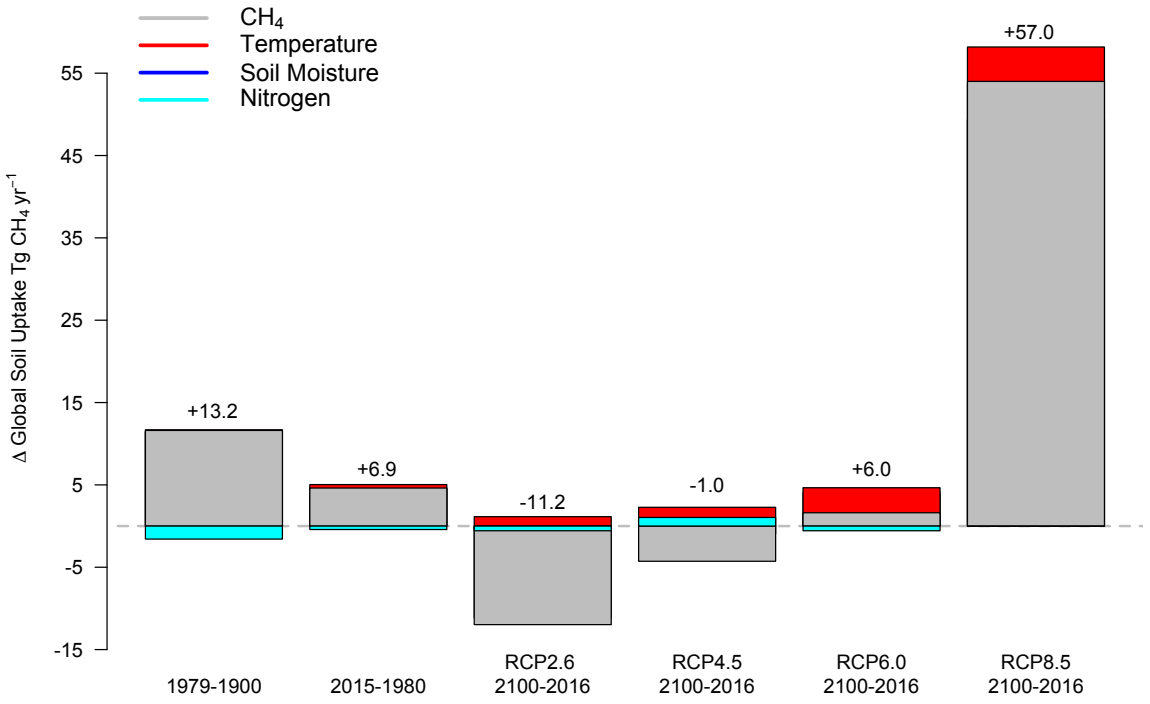

Figure 4.6 Change in global uptake of atmospheric CH_4 by soil (number on top of each bar in Tg CH_4 yr^{-1}). Predicted changes in uptake rates for the period 2016 to 2100 are shown for RCPs 2.6, 4.5, 6.0 and 8.5. Each bar is divided into the proportions of change attributed to the four main factors that drive soil methanotrophy: atmospheric CH_4 concentration, soil temperature, SM and N input (via deposition and fertilizers).

4.3.4 Drivers of change: Regional trends

A regional evaluation of the main driver of trends in the global CH_4 sink reveals differing patterns over different periods. During the early historical period, atmospheric CH_4 controlled the change in uptake across the globe (Figure 4.7a). However, during the late historical period, other factors started to become regionally important, especially temperature over the high latitudes and N over the regions with high agriculture intensity such as India, China and eastern Europe (Figure 4.7b).

In all RCPs, atmospheric CH_4 still dominates the regional trend over most of the planet, but temperature appears consistently as a key driver over the Northern Hemisphere (Figure 4.7 c, d, e, f). The influence of temperature has a larger extent in RCPs 4.5 and 6.0, which is consistent with the increase in the uptake over the high latitudes seen in Figure 4.4 (e, g). The effect of SM over those scenarios, seems to dominate regions over south America, and it is related with an increase in uptake seen in Figure 4.4 (e, g). T and SM become important in RCP 4.5 and 6.0 because they increase capacity of microbial community to increase the CH_4 consumption. Finally, the effect of the N inputs appears as a dominant driver over India, East Asia, North America and part of Europe and also there were a decrease over those regions observed in Figure 4.4 (e, g). Over those areas temperature and N may interact, in areas where N decreases and T increases the uptake increases even further.

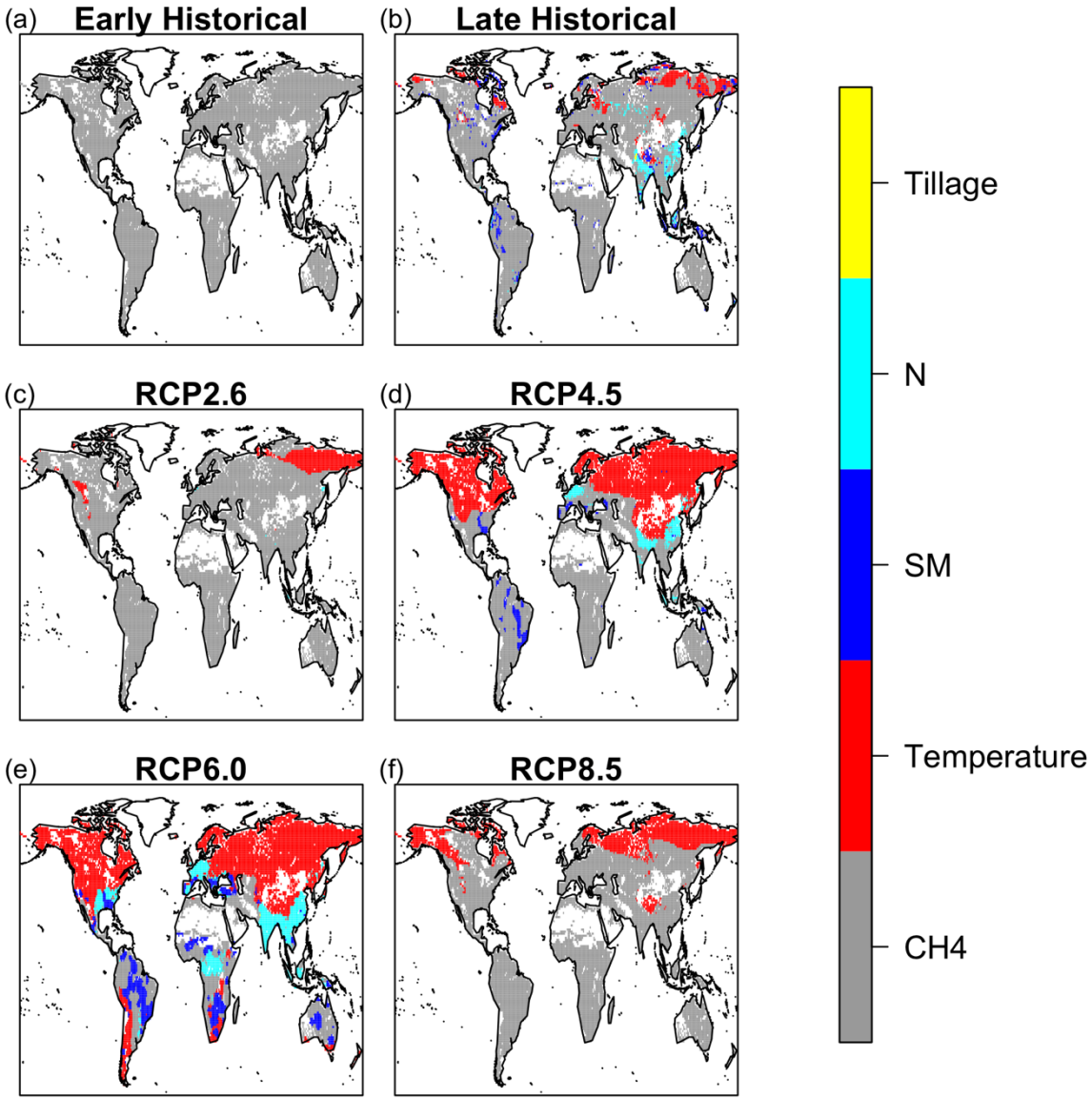

Figure 4.7 Spatial attribution of the main drivers of change in soil uptake of atmospheric CH_4 during (a) 1900 to 1979, (b) 1980 to 2015, and from 2065 to 2100 based upon (c) RCP2.6, (d) RCP4.5, (e) RCP6.0, and (f) RCP8.5. Color denotes the driving factor that accounts for the largest proportion of change in the temporal trend of soil CH_4 uptake rate in each grid cell. The change in CH_4 uptake by soil can be either positive or negative.

Three potential hypotheses are proposed to explain the increasing contribution of temperature to the uptake: increasing bacterial activity, larger uptake area due to thawing permafrost and longer active season. The first hypothesis is based on the increase in the enzymatic activity as a function of the increase in temperature. Several studies (Castro et al., 1995; Czepiel et al., 1995; Whalen & Reeburgh, 1996) showed that there is an optimum temperature for the maximum CH_4 oxidation rate around 28 ºC. Thus, for ecosystems and times when temperature is below the optimum, increasing temperatures in the future will result in higher uptake rates until the optimum is reached (Appendix C, Table C1.1). For example, if the temperature

increases globally by +5ºC, the tropical evergreen and deciduous forest would have a decrease of –2% and –4 % respectively in the uptake, because temperature would surpass the optimum. The second possibility is an increase in the area where uptake occurs due to thawing permafrost (Appendix C, Figure C1.2). The difference in the frozen soil area was estimated across the last three decades (1980-2015) and the end of the 21st century (2065-2100) and, depending on the RCP, the frozen soils could be reduced between 2.4 and 13.1 x10^{6} m^{-2}. Finally, the increase in temperature can also lead to an increase in the number of days with temperatures above freezing point, particularly in the NH, deriving in a longer bacterial activity season (Appendix C, Figure C1.3) (MeMo exhibits methanotrophic activity at temperatures above -5ºC). This mechanism can lead (depending on the RCP) to an increment between 14 to 62 additional days per year of uptake in the high latitudes and between 6 to 36 additional days in average globally. Lau et al., (2015) predicted an increase in the sink strength over 5-30 additional days as the Arctic warms by 5-15 ºC during the century (1990-2090). In summary, it is feasible that the effect of the temperature over the uptake will be the result of the three patterns suggested, leading to an increase in the CH_4 consumption for the oncoming years. Over the NH this the role of increasing temperature will become more important for the uptake as a main driver, than the increase in atmospheric CH_4 concentration.

In the case of the N inputs, the small patches where the future trend was dominated by this driver (most in RCPs 4.5 and 6.0) were also those with a large decrease in N inputs due to reforestation (Appendix C, Figure C2.1). Thus, by reducing the crop area by increasing forests, there is also a reduction in N inputs by fertilizers and an increase in the uptake. However, it is important to notice that when N is reduced the CH_4 soil uptake increases immediately in our model, yet several studies showed that the recuperation of the consumption of CH_4 by soils after the agricultural activity takes months to years (Mosier et al., 1991; King and Schnell, 1994; Hüstch et al., 1994; Tate, 2015; Yue et al. 2016). The above implies that while a reduction in the N input to the system will lead to an increase in the uptake, the recovery rate is likely to be slower that we are estimating here. Nevertheless, the recovery of the soil CH_4 sink after the addition of N inputs remains as one of the largest unknowns for most ecosystems.

Finally, across future scenarios the contribution of SM as a global average is minimal (Figure 4.6). A similar study by Zhuang et al., (2013), concluded that SM is not a major factor or CH_4 global uptake by soils for the last century. This can be explained by the response of the uptake to a decrease on SM (a drying trend), which is the general tendency in all RCP (Appendix C, Figure C3.1). Soil CH_4 uptake response to moisture has an optimum in

20%, which is consistent across different ecosystems worldwide and under laboratory conditions (Adamsen & King, 1993; Castro et al., 1995; Boeckx & Cleemput, 1996; Klemedtsson & Klemedtsson, 1997; Epstein et al., 1998; Van den Pol-van Dasselar et al., 1998; Burke et al., 1999; West et al., 1999; Mosier et al., 2002; McLain & Ahmann, 2008). Thus, drying or wetting soil can have either a positive or negative effect, for example, if SM decreases across arid regions the uptake declines as well, (Appendix C, Figure C3.3, red), while over wet regions a decrease in moisture leads to an increase in the uptake (Appendix C, Figure C3.3, green). This results in a net zero effect of changing moisture on the global soil uptake. This pattern is similar across the RCPs (Appendix C, Figure C3.3) because the arid and wet regions remain the same, with only a change in the drying magnitude (Appendix C, Figure C3.1). Another possible explanation is because ESM models show a large disagreement on the direction and intensity of the change in soil moisture by 2100 in all RCPs (Appendix C, Figure C3.2). This is particularly evident for RCP2.6 where high-confidence and agreement occurs in less than 10% of the global area, but even in RCP8.5, where the highest agreement occurs, the value is only 1/3 of the area. As a result, the centennial change in soil moisture in the model ensemble cancels out, leading to small changes (less than 5% for the whole century at a regional scale) that are unrepresentative of the variance induced by using multiple models. This leads to a reduced soil moisture signal on the CH_4 uptake, minimizing its impact on the process as a result of an average soil moisture change that resembles the present (i.e. no change in soil moisture in the future, due to model discrepancy, leads to no change in CH_4 uptake). In reality, current research shows that SM is likely the largest control of the CH_4 uptake across large regions, particularly in the northern hemisphere. An analysis using individual models could provide a more realistic impact of future changes in SM on the CH_4 uptake. However, due to the complexity of such analysis and time needed, it fells out of the scope of this chapter and was not included as part of the thesis.

On a regional scale, SM can be a dominant driver of the trend. This was the case over the arid regions on central Australia and central and south Africa, where there was a decrease in SM that led to a decreased uptake (Appendix C, Figure C3.3). On the contrary, over the wet regions on south and north America, and south Europe there were a decrease in SM that led to an increase in uptake (Appendix C, Figure C3.3). Additionally, the negative effect of increase SM and decrease uptake can be seen in the center of North America (Appendix C, Figure C3.3). The regional contribution of SM to the global trend can also be seen on the intermediate RCPs 4.5 and 6.0 (Figures 4.8 and Appendix C, Figure C3.3). These results are consistent to the findings of Bowden et al. (1998) (laboratory experiment), Blankinship et al. (2010) in an annual

grassland and Christiansen et al. (2016) on temperate rain forest, which found that the alterations in the SM are a fundamental factor over the changes in the soil CH_4 uptake. Also, in a recent paper Ni & Groffman, (2018) found a 77% mean decrease in the soil uptake by forest soils over North America due to the increase in precipitation for the last ten years. Therefore, it seems that SM is a primary driver of soil uptake under local and possibly regional conditions, however its impacts are balanced at a global scale and thus, acting as a minor driver of the global uptake flux.

4.4 Conclusions

The CH_4 uptake by soils increased almost doubled during last century (1900-2015). It is very likely that this tendency continues increasing in the remaining century. The size of this sink increased from consuming 8% of the human emissions in the early 20th century (1900-1979) to 10% by the end of the century (1980-2015) and will likely continue to increase in the future (up to 18% in RCP 2.6), because an acceleration of the biological activity that controls the flux. The main driver behind this increase has been atmospheric CH_4 concentration, however, over the last decades and over some future RCPs other factors have become more relevant, especially in RCPs 4.5 and 6.0. Particularly, the increase of global temperature led to higher CH_4 uptake over high latitudes, mainly due to three reasons: an enhancement of bacterial activity (increase of the enzymatic response to temperature), an increase in the surface (permafrost thawing) and a longer bacterial active season (increase in the number of days of methanotrophy during the year). Soil moisture will likely increase the uptake in regions that currently are wet and will decrease uptake in regions that currently are dry due to the expected decrease in humidity in the remaining century. Finally, nitrogen is possibly going to lead to an increase in uptake due to a reduction in the application of N-fertilizers as a consequence of large-scale reforestation in RCP4.5 Our results point out that the biological component of this sink has partially decoupled methanotrophy form its dependency of the atmospheric CH_4 concentration and in the future, the variation of other drivers will likely have a more crucial role. This has important implications in our understanding of the global CH_4 cycle and the role played by methanotrophy. Although the process has been neglected as a small part of the sink, a large increase in temperature, driven by CO_2 and other greenhouse gases, a decrease in nitrogen inputs (via reforestation) and a dryer world could all lead to a higher contribution to the total sink and a potential important mitigation option.

CHAPTER 5

CH_4 uptake by soils since the last glaciation maximum

5.1 Introduction

The air trapped in the ice cores has revealed the oscillations in the atmospheric CH_4 concentration and other important gases through the last 800,000 years (Petit et al. 1999, Loulergue et. al., 2008). The fluctuations in atmospheric CH_4 in tens of thousands of years can be explained by the changes in the Earth´s orbital changes (Loulergue et al., 2008). However, the mechanisms behind the fluctuations at millennial scale since the Last Glaciation Maximum (LGM) remain uncertain. Nevertheless, several model reconstructions of the period explain these changes as the result of variations in the equilibrium between the largest natural sources, the wetlands, and the largest natural sink, the oxidation by OH radicals in the troposphere, driven by climate variations (Levine et al., 2011; Quiquet et al., 2015; Yang et al., 2017; Hopcroft et al., 2017). These components of the global CH_4 cycle have been thoughtfully studied in the paleorecord (Ringeval et al., 2013; Valdes et al., 2005; Kaplan et al., 2006); however other components of the cycle remain uncharacterized, in particular the oxidation of CH_4 by soil bacteria, which is the only terrestrial sink of CH_4.

Methane oxidation by soil bacteria removed around 2% of the CH_4 that remained in the atmosphere during the last century (1900-2000), and it responsible for consumption of approximately 8% of the CH_4 emitted by human activities (as reported in Chapter 4). The process fluctuates with CH_4 concentration and climate (Zeng et al., 2018, Murguia-Flores et al. 2018), all of which varied greatly since the LGM. The main driver of methanotrophy is the concentration of CH_4 in the atmosphere and the diffusivity of the gas into soil, driven by the soil pore space and the water content. During the Holocene, the average concentration of CH_4 was 520 ppb with a minimum of 370 ppb in the last glaciation maximum (LGM) (21,000 years ago), a peak of 675 ppb during the early-Holocene and a decrease during mid-Holocene to 585 ppb, to finally rise again to its maximum of 722 ppb at the preindustrial era (AD1750) (Mitchell et al., 2013). The second factor that controls methanotrophy rates is temperature, which affects the enzyme responsible for the methanotrophic activity contained inside the methanotrophic bacteria. These microorganisms perform optimally in the range of 5 to 40 °C and their activity becomes minimal under freezing conditions (Castro et al., 1995; Dasselar, 1998; Mohanty, 2006). Land temperature increased by 3-5º C during the LGM to the preindustrial era (Shakun

et al., 2012), which also is expected affected to positively affect methanotrophy performance. Finally, both high and low precipitation or soil moisture content negatively affect methanotrophy, with an optimum occurring across semi-arid ecosystems (Singh 1997; Luo et al., 2013). Humidity in general has changed greatly globally, especially the estimations for soils moisture revealed an increase pattern through the last 21,000 years (Singarayer et al., 2011).

This millennial fluctuation of the main controllers of methanotrophy means that the process must have varied greatly, but only a few estimations are available. For example, Hopcroft et al., (2017) estimated a global uptake of 6 Tg CH_4 y^{-1} during the LGM to a maximum of 11 Tg CH_4 y^{-1} using the Earth System Model HadGEM2-ES and an offline scheme based on Curry (2007). Other authors assumed the soil uptake remained constant since the LGM and through the whole Holocene, using a reconstruction of vegetation, simulating a constant 10 Tg CH_4 y^{-1} (Chappellaz et al., 1993). Finally, some studies estimate the total soil sink to be less than 0.5 Tg at LGM (*e.g.* Kaplan et al. (2002) based on Ridgwell et al. (1999) model), arguing that the methanotrophy in upland soils was barely able to metabolize CH_4 from the atmosphere, due to the low CH_4 concentrations. Thus, in spite of our understanding of the underlaying drivers and their variation since the LGM, we have an incomplete understanding of the changes in the soil CH_4 sink.

Additionally, abrupt changes in the climate have occurred at millennial scale since the LGM and they have been recorded in ice cores from Greenland (Alley et al., 1993; Taylor et al., 1993). For example, one of the cases studied is the Younger Dryas, which was a sudden return to glacial temperatures in the North Atlantic region and the duration was almost a millennium during the last deglaciation (Alley et al., 1993; Dansgaard et al., 1989; Fairbanks 1989). Associated with this, the temperature varied greatly over Greenland during the last glacial period and these ups and downs in temperature, known as Dansgaard-Oeschger or D-O events (Dansgaard et al., 1984), occurred every 1500 years. They are characterized by an abrupt increase in temperature of as much as 10ºC in only a few decades, followed by a gradual return to cold glacial conditions. There is evidence that the CH_4 concentration in the atmosphere followed those fluctuations in temperature, and CH_4 changed by 50-200 pbv in less than a century during the D-O events (Baumgartner et al., 2014). Several studies have tried to determinate if thus abrupt changes in climate affected all the globe or only the North Atlantic region (Clement & Peterson, 2008). However, there is no evidence of how the atmospheric

CH_4 uptake by soils was affected by those changes as previous modelling studies of global methane cycle during this period did not consider the global soil uptake (Hopcroft et al., 2011, Ringeval et al., 2013).

Therefore, the aim of this chapter is to simulate the atmospheric CH_4 uptake by soils and the mechanism of its millennially changes since the LGM to the preindustrial era (AD1750). In order to achieve this, we asked the following questions:

1) How did atmospheric CH_4 uptake by soils changed from LGM (21Kybp) to preindustrial era (AD1750).
2) What is the atmospheric CH_4 fraction removed by global soils through this time period?
3) What are the mechanisms behind the variation of the soil CH_4 uptake in particular in relation to the atmospheric CH_4 concentration?
4) How did abrupt millennial scale climate changes impact atmospheric CH_4 uptake by soils?

5.2 Methods

5.2.1 The MeMo model

The process-based Methanotrophy Model (MeMo) (Murguia-Flores et al., 2018), a novel model to quantify atmospheric CH_4 uptake by soils was used to estimate the uptake from LGM to preindustrial era. The new analytical solution and revisited physical relationships proposed in MeMo are useful for the CH_4 uptake in the full profile and consist of two parts: 1) the CH_4 diffusion into the soil, controlled by the physical soil properties, soil moisture and temperature, and 2) the microbial CH_4 oxidation, based on a based oxidation rate (for an uncultivated and moist soil at 0°C), which is modified by temperature and soil moisture (for this chapter N input was not considered). The full description of the model is available in Murguia-Flores et al., (2018) (Chapter 2). Additionally, this model was successfully used to estimate the global annual global mean of atmospheric CH_4 uptake by soils (Chapter 2), the spatial and temporal dynamics of this sink (Chapter 3) and to estimate the main drivers of global uptake change and their contribution to the global budget, during the last century and for future scenarios (Chapter 4).

5.2.2 Driving data

The atmospheric CH_4 concentration, temperature at the surface and soil moisture data used to force our model were taken from Hadley Centre Climate Model, HadCM3M2 (Gordon et al., 2000), with basic description of the simulations in Singarayer & Valdez (2010). However, the new simulations were configured with the land mask, ice sheets and sea-level from ICE-6G_C (Peltier et al 2015). HadCM3M2 has a resolution of 3.75º in longitude and 2.5º in latitude.

The MeMo model was runed as slices of time every 1000 years, with the mean of 12 time-steps (simulated average months) for each factor: atmospheric CH_4, temperature and soil moisture, from Last Glaciation Maximum (LGM) to Preindustrial era (Figure 5.1). Bulk density and clay content for modern soils were used (Shangguan et al., 2014), the value of L was calculated using MeMo and the three variables were extrapolated from the nearest grid cells to account for the total land surface in the LGM. The deserts were masked using the mask of plant functional types (PFT) and selecting the provided by HadCM3M2. Different values of k_0 were used for forest, grasslands/savanna, tropical forest and the rest of the world as described in Chapter 2. The different k_0 values were imposed using the PFT fractions. Nitrogen input was not included in any time-period. In addition, to simulate the abrupt millennial-scale climate variations, due to the potential impact of a partial melting of the Greenland ice sheet from the LGM to preindustrial era, MeMo was run with temperature and soil moisture from Kageyama et al. (2013), where a simulation of freshwater flux is imposed in the North Atlantic to force variations in the Atlantic Meridional Overturning Circulation.

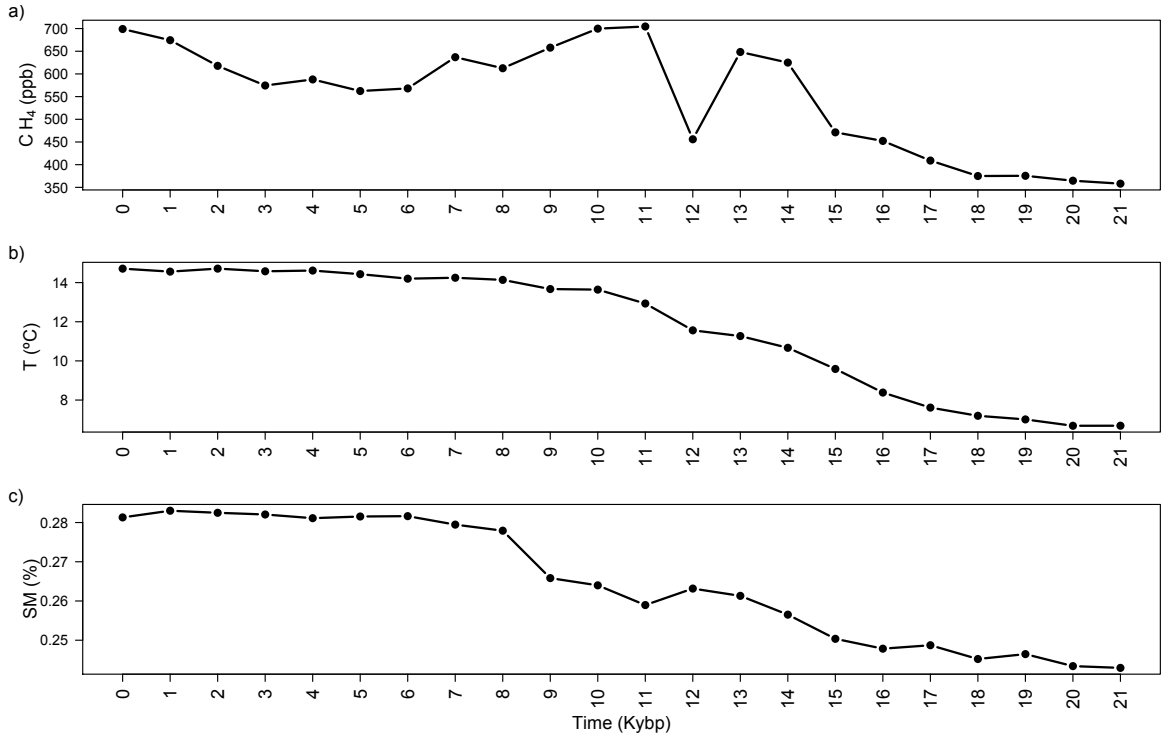

Figure 5.1 Driving data used to force the model in slices of time of 1000 years, from the LGM to the preindustrial era (slice of time 0). a) Atmospheric CH_4 concentration (ppb), b) Global mean land Temperature (ºC), c) Global mean soil moisture (%), provided by HadCM3M2 model.

5.2.3 Data Analysis

MeMo was run at a monthly resolution every 1000-year slices since LGM (21 kybp) to preindustrial era (0 kybp) to simulate the atmospheric CH_4 uptake by soils (264 timesteps). The maximum and minimum values of uptake were plotted to observe the main difference and the change in the land extension in Figure 5.3. Additionally, the fraction of uptake represents of the global budget was calculated through time. The main equation of MeMo was distillated to find the simplest explanation between both process: diffusion and microbial oxidation. Finally, the mechanism behind the constant fraction that uptake represent in the budget, were explained analyzing the main components of MeMo (diffusion and microbial oxidation and the factors that modified both).

A comparison between both simulations: an abrupt climate variation run and a smooth run (or without abrupt climate change) was conducted in order to determinate the impact of millennial scale climate variation on CH_4 uptake by soils. These are similar to results described by Singarayer & Valdes, (2010).

5.3 Results

5.3.1 CH_4 uptake by soils since LGM to preindustrial era

Figure 5.2 shows the temporal CH_4 uptake change since LGM to preindustrial era in slices of 1000 years. The soil flux increased from 6.8 to 17.2 $TgCH_4yr^{-1}$ from 21,000 years ago to the preindustrial era. This is likely driven by the coupled the variation with climate (increasing soil moisture and temperature) and the rise in atmospheric CH_4 concentration (Figure 5.1). However, there were some important millennial variation, in particular, the events with extreme soil uptake (positive and negative) were: 21Kybp the lowest uptake with 6.8 Tg CH_4 y^{-1}, a decrease 12 Kybp to 10.3 Tg CH_4 y^{-1}, a peak10 Kybp of 17.0 Tg CH_4 y^{-1} and a second peak in recent times to 17.2 Tg CH_4 y^{-1}.

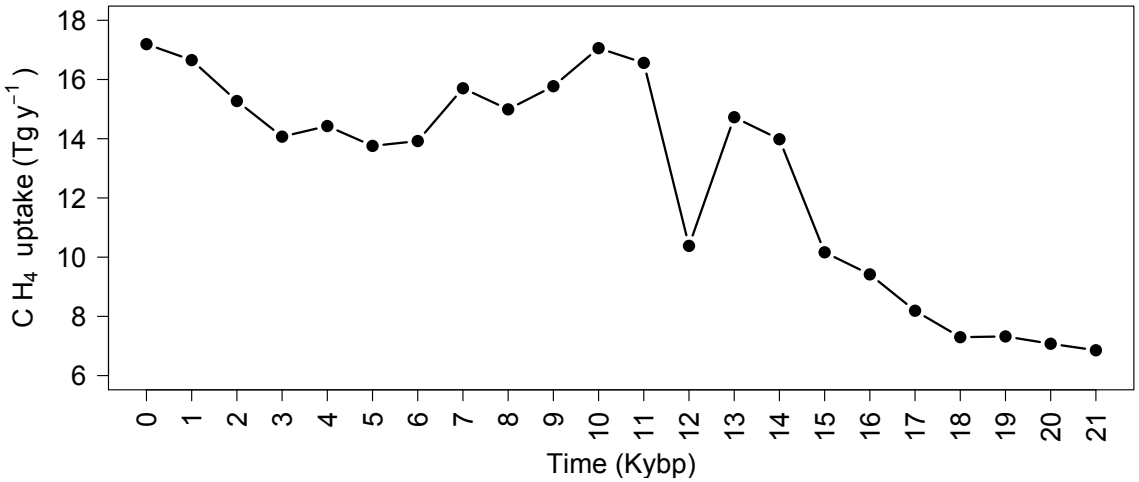

Figure 5.2 CH_4 uptake by soils every 1000 years since LGM (21Kybp) to preindustrial era (mg CH_4 m^{-2} y^{-1}) simulated using MeMo

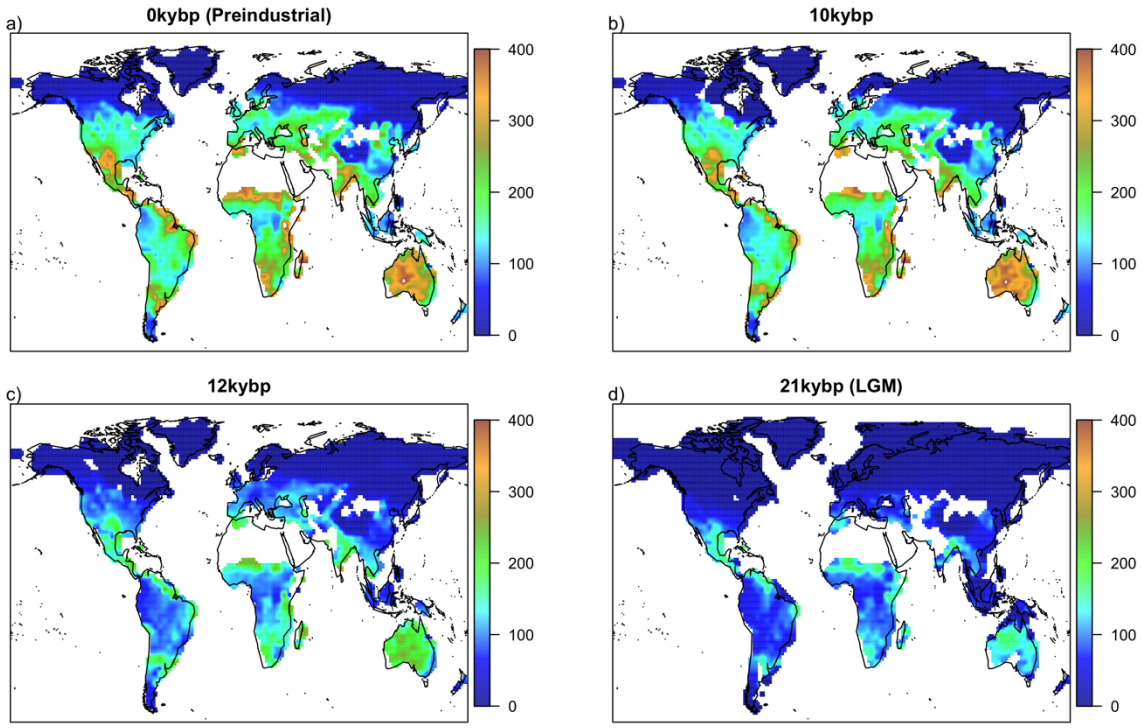

Figure 5.3 Annual gridded mean CH_4 uptake by soils (mg CH_4 m^{-2} y^{-1}) for four time slices. a) for preindustrial era (time slice 0 Kybp), b)10 Kybp, c) 12 Kybp and d) LGM (21 Kybp).

In order to understand the spatial variation across those four time slices we plotted the gridded mean of CH_4 uptake by soils (Figure 5.3), some strong spatial variations in the uptake through time. During the LGM (Figure 5.3 d) where low atmospheric CH_4 concentration, temperatures and soil moisture occurred, low uptake rates were simulated globally with the minor exception of some tropical regions. Similarly, an important decrease in the uptake was registered at 12 Kybp (Figure 5.3 c), possibly following the decrease in atmospheric CH_4 concentration. The maximum uptake rates were registered at 10 and 0 Kybp time slices with almost identical spatial signatures: both revealing the highest uptake rates occurring in the Southern Hemisphere, particularly in the dryer regions.

5.3.2 The CH_4 uptake in the global paleo-budget

In spite of the large temporal and spatial variation of the soil CH_4 uptake since the LGM, the fraction consumed relatively to atmospheric CH_4 remained remarkably constant (Figure 5.4). The uptake has represented a constant sink of 1% of the atmospheric CH_4 through the last 21,000 years, with practically no variation. This means that, in spite of changes in landcover, frozen area, temperature and humidity, the changes in the global uptake are practically linear in relation to the atmospheric CH_4 concentration.

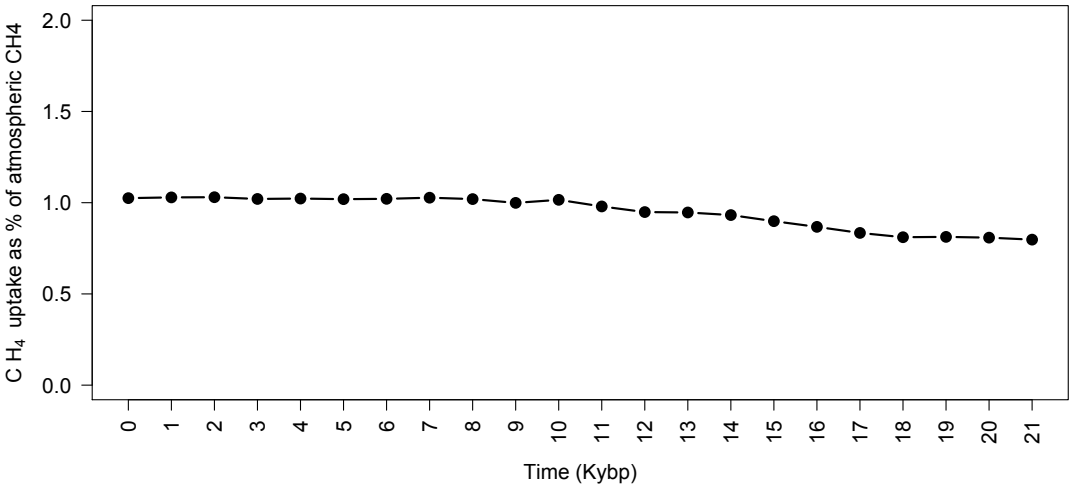

Figure 5.4 CH_4 uptake percentage of atmospheric CH_4 globally (uptake/atmospheric CH_4 concentration), in slices of 1000 years since LGM (21Kybp) to preindustrial era (0Kybp).

However, figure 5.5 shows that, regionally, the contribution of the tropics and the rest of the land is different and varies greatly over time. In particular, the contribution of the tropical land to the total uptake decreases with the increase of temperature and soil moisture through time, while the rest of the land increase its contribution with the same conditions.

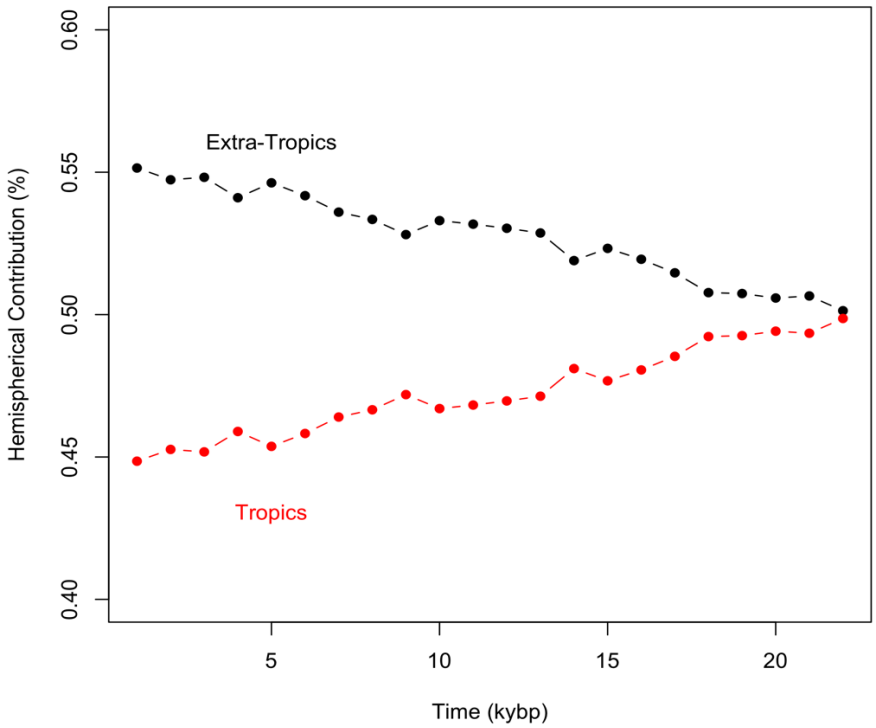

Figure 5.5 CH_4 uptake percentage of atmospheric CH_4 concentration in the tropics and the extra tropics (northern and southern high latitudes) in slices of 1000 years since LGM (21Kybp) to preindustrial era (0Kybp).

In the following section, the different aspects of our model (diffusion and oxidation) and in their components are separated in order to elucidate the reason behind the constant percentage that uptake represents of atmospheric CH_4 during this period (LGM-preindustrial).

The equation that describe MeMo v1.0 is as follows:

$$J_{CH4} = -D_{CH4}\left(-A\sqrt{\frac{k_d}{D_{CH4}}} + B\sqrt{\frac{k_d}{D_{CH4}}}\right) \quad (1)$$

Where: J_{CH4} is the uptake flux, D_{CH4} is the diffusion rate, k_d is the microbial oxidation rate and A and B are integration constants. Eq. 1 allows for (i) complete consumption of CH_4 within the soil interval, (ii) influx of CH_4 from beneath the soil profile (*e.g.*, from thawing permafrost or production of CH_4 in oxygen-depleted microsites in soil), and (iii) a minimum CH_4 concentration at which methanotrophy can occur in the soil column.

To simplify Eq. 1, in order to see the interaction of the process in the model, we have to assume a flux at an infinity depth (z) $\frac{dCH_4}{d_z}|_{z->\infty} = 0$, as follows:

$$J_{CH4} = -D_{CH4} * \frac{dCH4}{d_z}|_{z=0} = D_{CH4} * C_{CH4} * \sqrt{\frac{k_d}{D_{CH4}}} = \quad C_{CH4}\sqrt{D_{CH4}k_d} \quad (2)$$

Based on Figure 5.4, the ratio between uptake and atmospheric CH_4 (C_{CH4}) is almost constant (C), which is expressed as follows:

$$\frac{J_{CH4}}{C_{CH4}} \approx C \quad (3)$$

Rearranging Eq. 2.

$$\frac{J_{CH4}}{C_{CH4}} = \sqrt{k_d \cdot D_{CH4}} \quad (4)$$

Then, by substituting 4 in 3:

$$C = \sqrt{k_d \cdot D_{CH4}} \quad (5)$$

$$\therefore C \approx k_d \cdot D_{CH4} \quad (6)$$

Following Eq. 6, the constant C_{CH4}/J_{CH4} must be driven by a balance between k_d and D_{CH4}. Thus, every component of k_d and D_{CH4} was examined..

The CH_4 diffusion into soil is described as follows:

$$D_{CH4} = D_{0CH4} * G_T * G_{soil} \quad (7)$$

Where D_{0CH4} is a constant of CH_4 diffusivity in free air, G_T is the temperature effect on gas diffusivity and G_{soil} accounts for the effects of pore size, connectivity and tortuosity on gaseous diffusion described as: $G_{soil} = \Phi^{4/3}\left(\frac{\Phi-\theta}{\Phi}\right)^{1.5+3/b}$, where Φ is the porosity, θ is the water content and b is a function of clay content.

The microbial oxidation rate of CH_4 is described as:

$$k_d = k_0 * r_{SM} * r_T \quad (8)$$

Where k_0 is a base oxidation rate constant for an uncultivated moist soil at 0°C scaled by three factors to account for the influence of soil moisture (r_{SM}) and soil temperature (r_T).

Based on this disaggregation of the components, we plotted k_d, D_{CH4} and their particular components (G_T, G_{soil}, r_{SM} and r_T) (Figure 5.6). Interestingly, we found an opposite temporal pattern between k_d and D_{CH4}. The microbial oxidation rate (k_d) increased through time (Figure 5.6a), following a large increment in microbial activity due to higher global temperatures (Figure 5.6c) and a small increment due to higher soil moisture (Figure 5.6e). On the contrary, the diffusion component (D_{CH4}) decreased through time (Figure 5.6b), driven in its totality by the negative effect of the increased soil moisture that limits the diffusion of CH_4 into the soil (Figure 5.6f). Thus, over the last 21,000 years the uptake remained constant in terms of the global budget, due to a natural equilibrium between the positive effect of increase in temperature and the negative effect of CH_4 diffusivity into soil due to the increase in soil moisture.

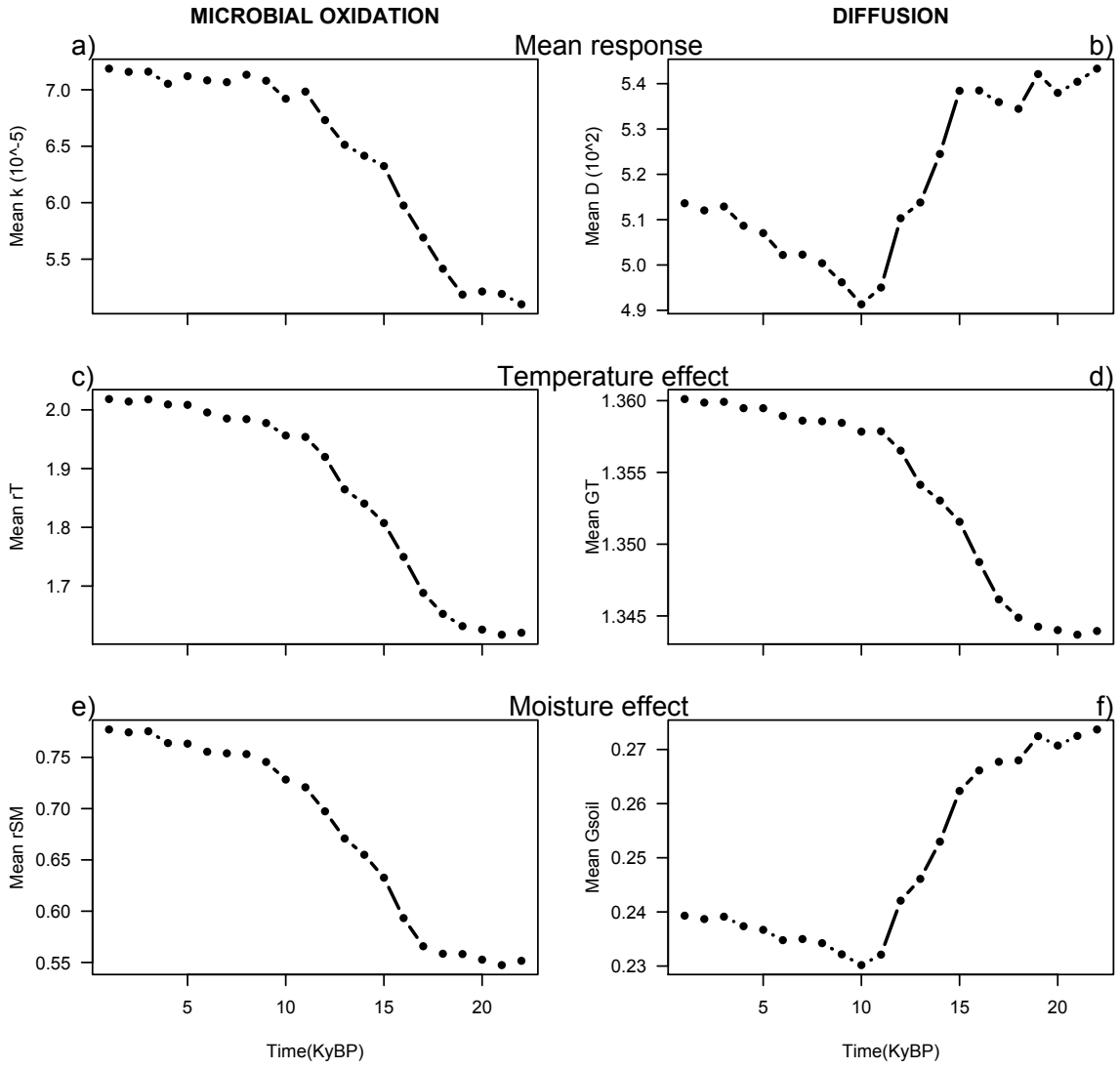

Figure 5.6 Time series for both processes involved in the CH_4 uptake by soils, microbial oxidation (a) and diffusion (b) from LGM (21Kybp) to the preindustrial era (0 Kybp). The individual components that modified the microbial oxidation through time, are showed in panel c) temperature response (r_T) and panel e) soil moisture response (r_{SM}). The components involved in the CH_4 diffusivity into soil are presented in panel d) temperature (G_T) and panel f) soil structure and water content (G_{Soil}).

To further visualize how this effect occurred spatially, we plotted the net change in the key components (r_T and G_{soil}) as the difference of the mean response in the Preindustrial era in relation to the LGM (Figure 5.7) for the Northern Hemisphere and the tropics. Our results show that the positive effect of temperature in the microbial activity is globally widespread but is much stronger over the NH. On the contrary, the negative effect of soil moisture in the diffusion occurs almost around previously frozen regions of the NH and a smaller negative effect is observed over SH, especially across the tropics and Australia (Figure 5.7).

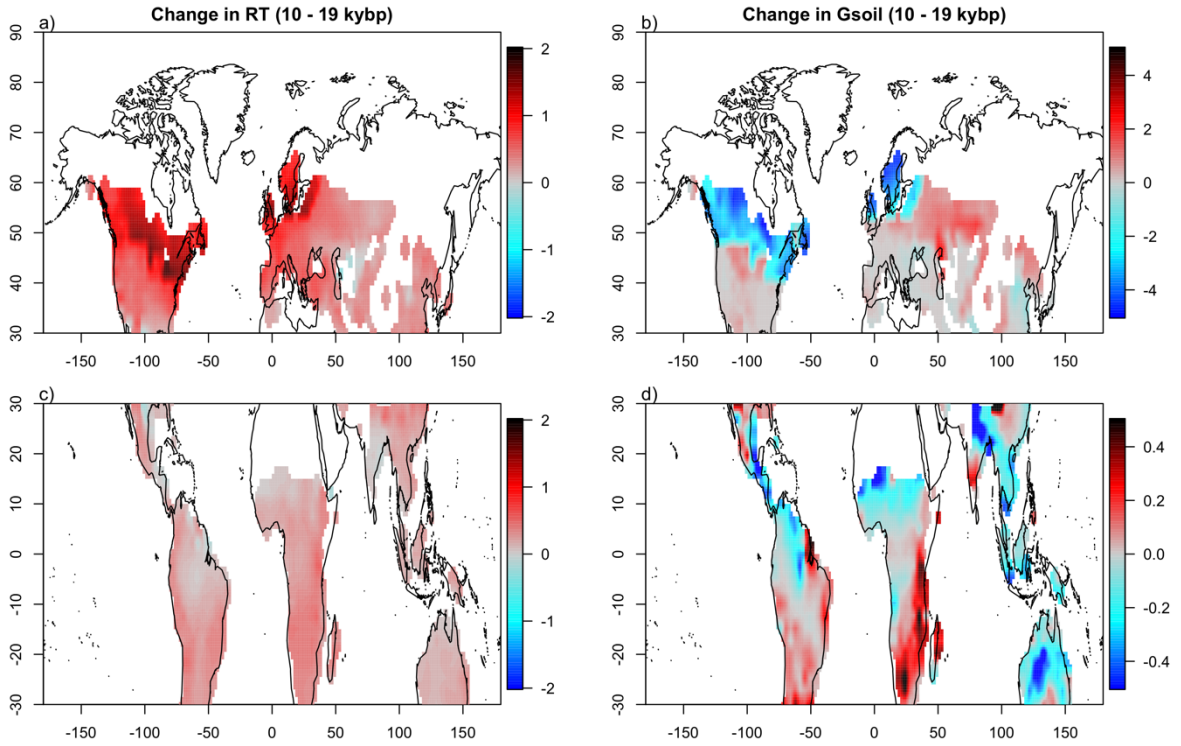

Figure 5.7 Change in gridded r_T (a) and G_{soil} (b) for the period 19Kybp - 10Kybp by hemisphere. The change en r_T and G_{soil} was calculated using the periods with the largest change in CH4 uptake and the differences were calculated as the period 10Kybp minus 19Kybp, regionally (Northern hemisphere and tropics). The globe is split in hemispheres as the change in Gsoil is an order of magnitude larger in the Northern hemisphere.

5.3.3 Response of the methane uptake to abrupt climate variations

Figure 5.8 shows the CH_4 uptake by soils simulated with both abrupt and smooth climate variations in a time series from LGM to preindustrial era. The simulated uptake with abrupt climate is slightly higher (1%), the abrupt climate simulated a CH_4 uptake of 7.2 Tg y^{-1} in the LGM and 17.4 Tg y^{-1} at preindustrial era, however there is not significant differences between simulations. As a result of the previous, the fraction of uptake with abrupt climate variations is still 1% from the atmospheric CH_4.

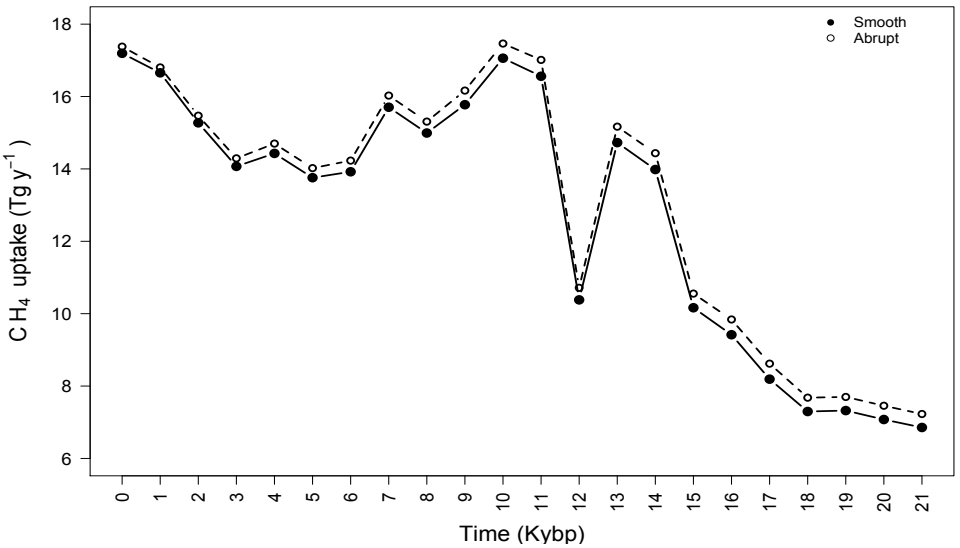

Figure 5.8 Response of atmospheric CH_4 uptake by soils to abrupt climate variations, simulated with both: smooth (solid line) and abrupt (dashed line) climate variations since LGM to preindustrial era.

However, in spite of globally average similar results, there are important regional differences. Figure 5.9 shows the spatial differences between the effect of abrupt vs smooth climate variations over the uptake. The wet tropical region consumed more uptake in the abrupt climate simulation (around 50%). While, the mid-latitudes (*i.e.* West Europe, USA and China) presented higher uptake with the smooth climate simulation. Those differences in both simulations follow the soil moisture distribution and the highest uptake rates were simulated where soil moisture decreased. The differences are as high as 80% of the total uptake between simulations and they were controlled by soil moisture. Nevertheless, the bipartite distribution of the spatial differences results in a similar global average of both simulations.

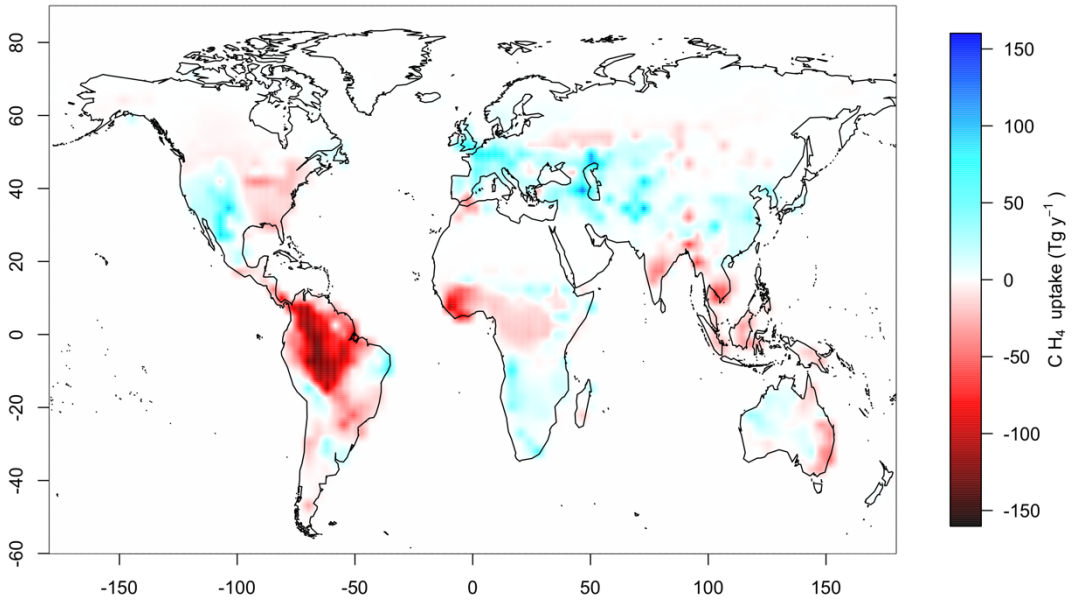

Figure 5.9 Differences in spatial response of CH_4 uptake by soils to abrupt climate variations, simulated with both smooth and abrupt climate (smooth minus abrupt) as the mean of the last 21,000 years. Higher uptake in the abrupt climate is represented by red regions located mostly in the wet tropics and high latitudes of the NH. Higher uptake in the smooth climate is represented by the blue regions, located particularly in the mid latitudes.

5.4 Discussion

The atmospheric CH_4 by soils varied with climate and atmospheric CH_4 concentration since the LGM to preindustrial era. Previous works assumed a constant uptake during the Holocene (*e.g.* Chappellaz, et al.,1993) or not uptake by methanotrophs at the LGM due to the low atmospheric CH_4 concentration (Kaplan, 2002). The uptake estimated at LGM (6.8 Tg y^{-1}) is consistent with previous model reconstructions, (*e.g.* 6 Tg y^{-1}; Hopcroft et al., 2017). Additionally, there was an increase in the uptake of around 40% from LGM to preindustrial era driven by the climate and CH_4 concentration. Based on these findings, it is clear that the atmospheric CH_4 uptake by soils cannot be considered to have a constant value (*i.e.* equal to pre-industrial) or to be zero during the LGM and later periods. However, our results did show that the fraction of CH_4 consumed by soils from the atmosphere has remained constant globally, around 1%. On the basis of these results, a relationship can be used to estimate CH_4 by soils at any time in the past, potentially during the whole of the past 800,000 years. This would be simply to take one percent of the total atmospheric concentration.

The temporal variations in the total mean global uptake can be explained by the variations in the drivers. The low uptake during the LGM was driven by the low CH_4 concentration, which in time decreased as a result of changes in both sources and sinks. The reduction in wetlands extension during the LGM could account for half of the reduction in CH_4, and the increase in the tropospheric sink (the CH_4 oxidation by OH radicals) is evoked to explain the remain of the reduction (Valdes et al., 2005; Kaplan et al., 2006). Additionally, low temperature and soil moisture led to low uptake rates globally, except in the tropics and central Australia, which had the highest uptake rates during this period (150 mg CH_4 m^{-2} y^{-1}).

During the next minimum (10.3 Tg y^{-1}) at around 12Kybp slice of time, there was an important reduction in the natural source of CH_4. The wetlands extension decreased in parallel with a cooling in Greenland, which forced the intertropical convergence zone to migrate southward, leading a reduction in the precipitation in northern tropical wetlands (Yang et al., 2017). This important reduction in atmospheric CH_4 led to the reduction in the global and regional uptake in particular in the NH.

The maximum value of uptake (17.0 Tg y^{-1}) before the preindustrial era occurred at around 10Kybp slice of time, which coincides with a peak in atmospheric CH_4 concentration. The rise in atmospheric CH_4 concentration during this period (11.5 to 9.0 kybp) could be explained by an increase in the sources, however the mechanisms are still under debate. Singarayer et al. (2011) propose an increase in the Southern Hemisphere tropical sources caused by a modification of seasonal precipitation due to a natural change in the Earth´s orbital configuration. Meanwhile Yang et al. (2017) proposed an increase in the emissions in the Northern Hemisphere extratropical regions (30-90º N) by 5%, following the temperature rise. In spite of which one happened, this increase in atmospheric CH_4 concentration and temperature lead to a peak in CH_4 consumption by soils, during this slice of time.

Finally, the increase in the uptake at preindustrial era is related with the increase in CH_4 and temperature. This increment in CH_4 is also in discussion, as some authors have suggested that agricultural activities and population started to influence the global atmospheric concentration (Ruddiman et al., 2008). However, Singarayer et al. (2011), showed that the early agricultural activity during this period is not necessary to explain the increase in methane, and attributed the change to the increase in the emissions from the wetlands in the Southern Hemisphere tropics. This significant increase in CH_4 concentration and temperature led to high uptake rates by soils.

Interestingly, in spite of all previous variations in climate and CH_4 concentrations, the fraction of atmospheric CH_4 consumed by the soils remained remarkably constant at global

scale. This is explained by a balance of the positive impact from the rise in temperature and the negative impact from the increase in global soil moisture. On the one hand, higher temperatures (*i.e.* from LGM to the preindustrial) led to an increment in bacterial activity and a widespread higher CH_4 consumption. On the other hand, the increase in global mean soil moisture decreased the CH_4 diffusion into the soil and consequently reduced the uptake. The magnitude and impact of the changes in moisture are different between the NH and the tropics. Moisture changes are larger in the NH, likely a result of the increase in global temperature and moisture transport is increased to the high latitudes (Yang et al., 2017) but its impacts on the uptake are likely smaller (due to the cold conditions limiting the uptake). On the opposite, there was a smaller increase of soil moisture over the tropics during late Holocene, caused by a change in the precipitation pattern due to a natural change in the Earth´s orbital configuration (O'Brien et al., 1995; Singarayer et al., 2011), which reduced diffusion as well and likely had a greater impact on the global uptake because this region consumed CH_4 throughout the whole time period.

When temperature increases, it leads to an increment in the bacterial activity and a higher CH_4 consumption. However, the increase of soil moisture also leads to a diminish in CH_4 diffusion in the soil, decreasing the net uptake rate. Thus, both processes balanced each other, resulting in a constant fraction of CH_4 removed from the atmosphere and no climate signal to appear in the global CH_4 uptake. The effect is particularly evident on the largest change in conditions of the time series (19-10 Kybp). At 21-19 kybp predominated a cooler and dryer climate (Valdes et al., 2005). On the one hand, the cooler climate inhibited the methanotrophs metabolism leading to slower consumption rates, while on the other hand, the dryer soils favoured the CH_4 diffusivity into soil (Whalen & Reeburgh, 1996; Crill et al., 1994). On the opposite extreme, from 10-0 Kybp, the climatic conditions changed, and both temperature and soil moisture increased. Higher temperature led to more rapid bacterial metabolism, but higher soil moisture decreased the CH_4 diffusivity into soil. As a result, in spite of the clear opposite climatic conditions, soil CH_4 consumption remained constant in relation to the global budget.

Interestingly, our results show that even when assuming abrupt changes in climate the fraction of atmosphere CH_4 consumed by soil methanotrophy remains the same. In particular, both model runs had remarkably similar global means, but with large spatial differences. In other words, the global uptake is distributed differently, driven by the inverse spatial impact of soil moisture. In the abrupt runs, a drier tropic is modelled with higher uptake rates and wetter conditions on the NH are present leading to lower CH_4 consumption. The pattern is the opposite

in the smooth runs. Thus, while there are large differences in the hemisphere contribution to the global uptake (up to 80%) the global value remains the same.

5.5 Conclusions

Atmospheric CH_4 uptake by soils was modelled for the last 21,000 years. The simulations indicated an absolute increase in the global value of uptake from LGM to preindustrial era, which follows a rise in temperature and atmospheric CH_4 concentration. However, the fraction of atmospheric CH_4 consumed by the soils remained remarkably constant through time. It was shown, that this was driven by a balance between the positive effect of the increased temperature and the negative effect of the increased soil moisture, resulting in a zero-sum effect of the climate on the uptake. Although, globally we could assume the uptake to represent a constant fraction of the global atmospheric CH_4 burden over the last 21,000 years, regionally there is great temporal variation, which can only be accounted by a dynamical model. Thus, this simple ratio cannot be extrapolated to a time-scale before or after the time period studied here (LGM-Preindustrial) and a process-based modeling approach (i.e. MeMo) needs to be done to obtain a more realistic value.

Finally, to understand the coupling/decoupling between the uptake and the atmospheric CH_4, two fundamental drivers of the process need to be accounted for: the climate -particularly temperature - and the atmospheric CH_4 concentration, both of which evolve through time.

In the paleo-record, all three variables -temperature, atmospheric CH_4 and uptake- evolved similarly. For example, if temperature increased (i.e. because of Milankovitch Cycles), atmospheric CH_4 concentration would increase as well (as the result of a combination of factors: higher ice-free land surface in the Northern Hemisphere (Petit et al., 1999), a larger extent of flooded areas and warming-enhanced biological activity of methanogens) and so would the uptake (due to higher atmospheric CH_4 concentration and temperature). Thus, all three (climate, concentration and uptake) were varying together, which led to a constant global soil uptake in relation to the atmosphere (1%).

However, the rise of anthropogenic fossil fuel emissions and the increase in temperature caused the system to disengage. In particular, because the increase in temperature is not driven only by changes in atmospheric CH_4 but mainly because the large increase in atmospheric CO_2 and other greenhouse gases. This has pushed the uptake to increase faster (due to higher bacterial activity) than the rate of increment of the atmospheric CH_4 burden. As a result, the soil CH_4 uptake is consuming a larger proportion of total atmospheric CH_4 concentration (1.8%) and in

warmer scenarios it could be even higher (2.4%). Thus, although CH_4 uptake by soils is potentially beneficial as a mitigation strategy, this high-uptake ratio is novel since the last LGM and likely in the history of our planet.

CHAPTER 6. Conclusions

6.1 Main findings

MeMo was developed to quantitatively estimate the uptake of atmospheric CH_4 by soil. This model improved the representation of the uptake flux in comparison with previous models. Additionally, the reparameterization of the main component in the light of recent observed measurements (*i.e.* the negative effect of soil moisture over microbial oxidation and a more realistic inhibition effect of nitrogen input via deposition and fertilizers) provides a tool to understand the changes in this process at global scale, and for past and future climate. For the first time, a process-based model to estimate global uptake was compared against observational data, performing a closer latitudinal distribution than previous models.

Atmospheric CH_4 uptake by soils is estimated by MeMo as an average annual global flux of 33.5 ± 0.6 Tg CH_4 y^{-1} for the period 1990 to 2009. The subtropical zone in the NH (20°-40° N) was the region with the highest uptake rates and tropical deciduous forest and dense open shrubland were the most efficient soil sink. Interestingly, uptake increased and almost doubled during the last century from 17 Tg CH_4 y^{-1} at the beginning of the century (1900) to 35 Tg CH_4 y^{-1} in 2015. This represents a mean acceleration of the process of 0.1 Tg CH_4 y^{-2}. In the remaining part of the current century, and depending of human activities, it could further increase to 82.7 Tg CH_4 y^{-1} in the most extreme scenario (RCP8.5).

In order to explain these changes, the main drivers of the process were explored in Chapter 4, where is shown that atmospheric CH_4 concentration was the main driver of change in the last century; however, other factors such as temperature, soil moisture and nitrogen started to play a more significant role and more so across future scenarios. In that sense, the decrease in nitrogen inputs could lead an increase in the uptake, driven due to a reduction in the cropland area. On the other hand, temperature could be responsible for an increase in the uptake across recent years and over future scenarios, due to three possible reasons: a reduction of frozen area on high latitudes, an increase in the number during a year with favourable temperature for methanotrophy and higher microbial activity across the planet.

Additionally, results shown in Chapter 5 it was shown that the soil CH4 sink has increased from LGM, it rose from 7 Tg y^{-1} 21,000 years ago to 17 Tg y^{-1} at the beginning of preindustrial era, varying with atmospheric CH4 concentration and climate. However, the fraction of atmospheric CH_4 removed by methanotrophy remained constant at 1%. The main reason behind this constant fraction is the balance between the effects of increasing temperature

and soil moisture over the global uptake, as the positive effect of temperature over microbial oxidation counteract the negative effect of soil moisture over CH4 diffusivity into soil, resulting in a constant 1% of the total atmospheric CH4 at any time from LGM to preindustrial era.

As a result of the previous, the role that methanotrophy plays in the global CH_4 budget has become larger. During the last 21,000 years the fraction of atmospheric CH_4 removed by methanotrophy remained constant at 1%. In the last century it increased to 1.8% and it is expected to increase up to 2-2.4% until 2100. Additionally, the ratio of CH_4 uptake by soils in comparison with total CH_4 emissions has increased from 4.8% in 1900 to 6.1% in 2015 and respect to human emission changed from 8.3% (in 1900) to 10.3% (in 2015), and it could represent 6.6-7.3% to the total CH_4 emissions and 9-18% of the human CH_4 emissions by the year 2100. Thus, these results show that soils are consuming a larger amount of CH_4 from the atmosphere and they are growing in importance in the context of the global budget.

The general conclusion of my PhD thesis is thus that CH_4 oxidation by soils has increased through time and its relative significance for the global methane budget is thus increasing, therefore, it is important to include soil CH_4 uptake in any Earth System model to improve the representation of the global CH_4 cycle, as well as future warming projections.

6.2 The understanding and modelling of key controlling mechanism of the soil methane uptake.

Different drivers interact to modify the soils methane uptake. In particular, this thesis focuses on atmospheric CH_4 concentration, temperature, soils moisture and nitrogen inputs. This section highlights how the modelling of each driving factor improved with this thesis and how it helped our understanding of the regional and temporal global soil CH_4 consumption.

6.2.1 Temperature

The temperature effect over CH_4 uptake and its improved representation was revised in Chapter 1. In particular, a new equation for the temperature response of the uptake under freezing conditions was developed, allowing for a small flux to occur up to -10ºC as indicated by recent findings. As a result, the coldest regions of the planet had higher CH_4 uptake rates than previously reported (as shown in Chapter 3). This new modelled structure allowed the exploration of the impact of future temperature change in the uptake and showed an increase in the number of days with active methanotrophy across the Northern Hemisphere. On the

contrary, over already hot regions (tropics) global warming could have a negative effect in the uptake. Finally, an increasing contribution of temperature to the total uptake trend was also found. Temperature led to an increment of 1.3 Tg of CH_4 or 10% of the total change during the early 20th century (1900-1979), to 0.9 Tg of CH_4 or 18% of the total change in recent decades (1980-2015) and between 10-50% of the total change in future RCPs. The effect of temperature on the global methane uptake increased in importance during the late 20th century over the northern hemisphere, due to the increase of methanotrophs metabolism. A similar effect can be expected in future scenarios, where even though CH_4 emissions are stabilized, temperature continues to increase as a result of CO_2 emissions.

6.2.2 Soil moisture

The soil moisture impact over CH_4 uptake was also revised. A novel parameterization and model structure were included, for a negative effect of high moisture on microbial activity over wet areas (Chapter 2). It allowed the estimation of CH_4 uptake in regions with both low soil moisture and high soil moisture, while previous models were forced to mask wetlands and wet regions and did not simulate uptake in these areas. This novel approach improved greatly the estimation of the flux over the tropics and revealed that arid regions have higher uptake rates than their wetter counterparts (Chapter 3). As a result, simulated global uptake patterns are in better agreement with observations reducing the total error. Finally, despite the future decrease in soil moisture across all RCPs, global uptake remains unaffected by the increase in drying conditions. This is the result of the balance between a smaller uptake across arid regions and increase across the wet.

6.2.3 Nitrogen

In the model developed in chapter 1, the direct and negative effect of nitrogen inputs on the global soil CH_4 uptake were included, parameterized and calculated. The work included the quantification of the effect of two different nitrogen sources: deposition and, for the first time, the input via inorganic fertilizer. This represents a major advance in comparison with previous models of the same family, which used the agricultural fraction as a proxy of the nitrogen effect. As a result, the modelled uptake was reduced by 1.4 Tg y^{-1} (4%) globally due to the negative impact of N inputs, and regions with the largest extension of cropland areas, such as India, Europe and North America are the most affected by it. Finally, in future scenarios, a

decrease in N inputs via reforestation could potentially drive a positive change in the uptake regionally and globally –particularly in RCP4.5-.

6.3 Limitations

Although the modelling and understanding of the global CH_4 uptake was improved with this thesis, there are important limitations useful for identifying future research directions that can be targeted with specifically designed experiments and model developments. They can be divided in three different types: parametrical, structural and driving data limitations.

6.3.1 Parametrical limitations

One of the key elements in the model is the usage of k_0 or the base microbial oxidation rate. Four different values of k_0 were used in Chapter 1, for four different ecosystems: grasslands, forest, tropical forest and the rest of the world. These values are based on long term direct measurements over the corresponding ecosystem types and represent and advance in comparison to previous models, which assume a single k_0 value across the globe. However, most biomes cannot be specifically represented because the lack of measurements.

A second important model structure limitation, is the Q_{10} value, used to calculate the effect of temperature on the microbial activity. Based on several recent publications, the parameterization of this equation was updated in MeMo, however, just like in previous models, only a single value for the entire planet was used. In contrast, recent findings have shown that the Q_{10} value varies across ecosystems, for instance higher Q_{10} values have been found over high latitudes in contrast with the tropics. Thus, this biome-level parameterization is still required to account for a more accurate estimation of the uptake and a better representation of future trends in the uptake in relation to global warming.

Finally, the inhibitory effect of N on the uptake was revised and a linear negative ration was proposed. Although the parameterization was based on several laboratory and field measurements, the percentage needs to be revised and compared with realistic simulations and experiments in order to improve its determination.

6.3.2 Structural model limitations

MeMo represents an advance of existing global soil uptake models, however, there are several structural components that could be improved or added, including:

- The recovery time once N-inputs are reduced or removed: no long-term effects of N addition to the uptake were assumed in MeMo (Chapter 1) and once N inputs stop the uptake immediately raises to pre-input values. However, long-term fertilization experiments have shown that methanotrophic bacteria populations take months or years to recover, just like the uptake. This effect could be included to improve global estimations in future scenarios.
- The effect of tillage: the direct physical effect of land use through tillage over bulk density are also modelled, which leads to a change in soil porosity and soil water-air balance. Model results indicate that the effect of tillage on the uptake was minimal. However, the model description of tillage should be revised with our growing understanding of the effects of tillage on soil structure and CH_4 oxidation to improve our understanding of the global uptake.
- The inclusion of additional driving factors such as, CO_2, pH and roots dynamics: all of these factors have shown to play an important role in regulating the uptake under particular conditions, such as ecosystem type, land use change and soil type. In spite of the previous, these factors have not been considered in any global model and could help to refine and improve the model performance in local uptake estimates.
- The inclusion of the biodiversity in the methanotrophs community (type I and type II bacteria): this could give us specific information about the uptake rate flux in aspects like, the positive effect of N, the effect of land use change, fire or other human alterations to the soil.

6.3.3 Driving data limitations

The data used to run the simulations have their own level of uncertainty. For example, a large proportion of the of the climatic data collected from meteorological stations to create global climatic products is relatively recent, and remote sensing using satellites started at the end of the 1980s. Nitrogen deposition data are only available from model simulations and nitrogen from fertilizers are national-level estimates. In addition, there is a lack of climatic representation in inaccessible areas, such as the Amazon and tropical forest in Africa. As a result, when a global climate product is built, different assumptions have to be made, leading to important difference across them. Thus, a key missing step would be to evaluate the level of variation in global CH_4 uptake estimates when comparing the same model but forced with different datasets.

On a similar note, there is a void of direct long-term CH_4 uptake observations across different ecosystems of our planet, limiting our capability to validate model results. In Chapter 1 global data of several process-based models against a large extent of field measurements was compared, but the highest degree of validation possible was only latitudinal every 10º. Clearly, this is not enough to estimate the level of error across the models in different ecosystems or with variable biophysical conditions.

6.4 Future research of the global CH_4 uptake by soils.

It is evident that further quantitative analysis of atmospheric CH_4 uptake by soils is necessary. The modeling approach applied in this thesis could provide direction for future studies to generate new specific data and generate new insights of key missing elements of our understanding of the CH_4 uptake by soils. I suggest new research based on three scales/methodologies of measurement: laboratory, field and modelling.

- Laboratory experiments: One of the gaps in our understanding and modeling the atmospheric CH_4 uptake by soils is the usage of Q_{10} and k_0 values for different ecosystems. Both of those are a key parameter in global methanotrophy models and can only be measured directly under laboratory experimental conditions.
- Field measurements: One point that was evident while building the model, was the need to validate the results against field observations. A large extent of small-scale fast measurements are available, but remarkably there is a lack of long-term (at least a year) measurements paired with climatic data that could be used to validate the model.
- Finally, the model we developed was improved structurally. This was discussed above, but it would be possible to include the capacity of microorganisms to discriminate atmospheric CH_4 from different sources using of isotopic signatures. This would allow exploration of the effects of the different CH_4 sources on uptake.

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Appendix A

A1.1 Depth diffusivity flux

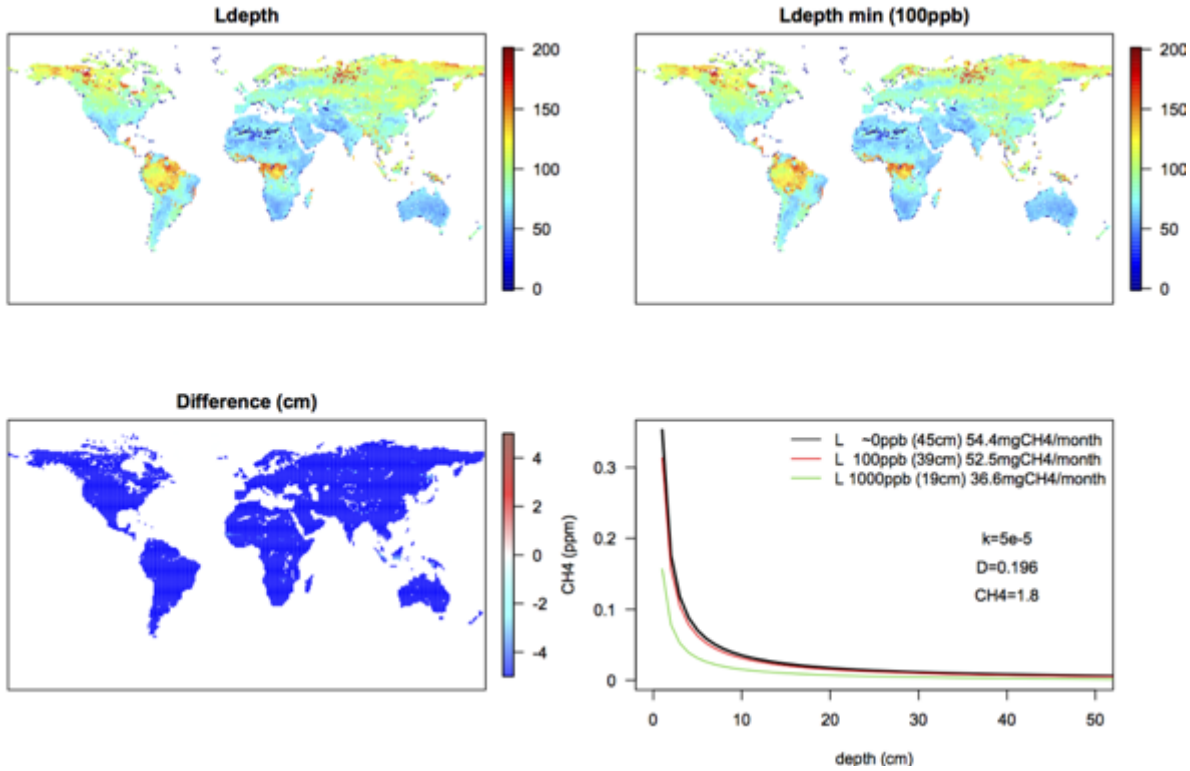

Figure A1: Comparison of model-derived depth L when CH_4(L)=0 (top left), CH_4 (L) = 0.1 ppm (top right), the difference in depth L using the two approaches (bottom left), and CH_4 consumption profiles in soil and total uptake flux using fixed parameters of k, D and CH_4 (bottom right).

A2.1 Observations used to construct r_{SM}, r_T and r_N.

Table A2.1 Observations used to construct r_{SM} based on the response of the CH_4 soil uptake to soil moisture in different ecosystems.

Author	Ecosystem	Location	Soil Moisture % w/w	CH_4 oxidation (mg CH_4 m^{-2} day^{-1})	r_{SM}
Adamsen & King, 1993	Subartic forest	54°43'N,66°42'W	10	0.8	0.53
Adamsen & King, 1993	Subartic forest	54°43'N,66°42'W	20	1.5	1.00
Adamsen & King, 1993	Subartic forest	54°43'N,66°42'W	30	0.7	0.47
Adamsen & King, 1993	Subartic forest	54°43'N,66°42'W	40	0.3	0.20
Castro et al., 1995	Temperate forest	42°30′N,72°10′W	20	6.0	1.00
Castro et al., 1995	Temperate forest	42°30′N,72°10′W	40	4.8	0.80
Castro et al., 1995	Temperate forest	42°30′N,72°10′W	60	2.4	0.40
Castro et al., 1995	Temperate forest	42°30′N,72°10′W	100	0	0.00
Whalen and Reeburgh, 1996	Boreal forest	64°N, 148°N	10	0.96	0.31
Whalen and Reeburgh, 1996	Boreal forest	64°N, 148°N	20	1.68	0.54
Whalen and Reeburgh, 1996	Boreal forest	64°N, 148°N	30	2.64	0.85
Whalen and Reeburgh, 1996	Boreal forest	64°N, 148°N	40	3.12	1.00
Whalen and Reeburgh, 1996	Boreal forest	64°N, 148°N	60	2.14	0.69
Whalen and Reeburgh, 1996	Boreal forest	64°N, 148°N	80	0.7	0.22
Singh et al., 1997	Dry tropical forest	25°N, 83°E	5	0.22	0.27
Singh et al., 1997	Dry tropical forest	25°N, 83°E	7	0.41	0.51
Singh et al., 1997	Dry tropical forest	25°N, 83°E	8	0.59	0.73
Singh et al., 1997	Dry tropical forest	25°N, 83°E	10	0.81	1.00
Singh et al., 1997	Dry tropical forest	25°N, 83°E	12	0.6	0.74
Singh et al., 1997	Dry tropical forest	25°N, 83°E	14	0.25	0.31
Singh et al., 1997	Dry tropical forest	25°N, 83°E	18	0.18	0.22
Dasselaar et al., 1998	Grassland	52°09′N, 5°5′E	16	0.2	0.25
Dasselaar et al., 1998	Grassland	52°09′N, 5°5′E	19	0.6	0.75
Dasselaar et al., 1998	Grassland	52°09′N, 5°5′E	21	0.7	0.88
Dasselaar et al., 1998	Grassland	52°09′N, 5°5′E	23	0.8	1.00
Dasselaar et al., 1998	Grassland	52°09′N, 5°5′E	25	0.5	0.63
Dasselaar et al., 1998	Grassland	52°09′N, 5°5′E	27	0.4	0.50
Dasselaar et al., 1998	Grassland	52°09′N, 5°5′E	29	0.3	0.38
Dasselaar et al., 1998	Grassland	52°09′N, 5°5′E	33	0.1	0.13
Tate et al., 2007	Temperate forest	39°33′S,175°41′E	10	0.24	0.25
Tate et al., 2007	Temperate forest	39°33′S,175°41′E	20	0.72	0.75
Tate et al., 2007	Temperate forest	39°33′S,175°41′E	40	0.96	1.00
Tate et al., 2007	Temperate forest	39°33′S,175°41′E	60	0.72	0.75
Tate et al., 2007	Temperate forest	39°33′S,175°41′E	70	0.48	0.50
Lau et al., 2015	Tundra	79°24′N,90°45′W	33	0.73	1.00
Lau et al., 2015	Tundra	79°24′N,90°45′W	66	0.11	0.15
Lau et al., 2015	Tundra	79°24′N,90°45′W	100	0.08	0.11

Table A2.2 Observations used to construct r_T based on the response of the CH_4 soil uptake to temperature in different ecosystems.

Author	Ecosystem	Location	Temperature (°C)	CH4 oxidation (mg CH_4 m^{-2} day^{-1})	r_T
Whalen et al., 1990	Landfill cover soil	37°N, 122°W	5	18	1.60
Whalen et al., 1990	Landfill cover soil	37°N, 122°W	10	30	2.00
Whalen et al., 1990	Landfill cover soil	37°N, 122°W	15	48	2.60
Whalen et al., 1990	Landfill cover soil	37°N, 122°W	20	50	2.67
Whalen et al., 1990	Landfill cover soil	37°N, 122°W	30	65	3.17
Whalen et al., 1990	Landfill cover soil	37°N, 122°W	35	70	3.33
Whalen et al., 1990	Landfill cover soil	37°N, 122°W	45	0	1.00
Dunfield et al., 1993	Subartic peat soil	45°14′N, 78°53′W	0	10	1.25
Dunfield et al., 1993	Subartic peat soil	45°14′N, 78°53′W	5	40	2.00
Dunfield et al., 1993	Subartic peat soil	45°14′N, 78°53′W	10	55	2.38
Dunfield et al., 1993	Subartic peat soil	45°14′N, 78°53′W	15	88	3.20
Dunfield et al., 1993	Subartic peat soil	45°14′N, 78°53′W	20	90	3.25
Dunfield et al., 1993	Subartic peat soil	45°14′N, 78°53′W	25	85	3.13
Dunfield et al., 1993	Subartic peat soil	45°14′N, 78°53′W	30	60	2.50
King and Adamsen, 1992	Temperate forest	54°43′ N, 66° 42′W	5	0	1.00
King and Adamsen, 1992	Temperate forest	54°43′ N, 66° 42′W	10	0.35	2.00
King and Adamsen, 1992	Temperate forest	54°43′ N, 66° 42′W	20	0.8	3.29
King and Adamsen, 1992	Temperate forest	54°43′ N, 66° 42′W	30	1.07	4.06
King and Adamsen, 1992	Temperate forest	54°43′ N, 66° 42′W	40	1.07	4.06
King and Adamsen, 1992	Temperate forest	54°43′ N, 66° 42′W	45	0	1.00
Castro et al., 1995	Temperate forest	42° 30′N, 72°10′W	-5	0.35	0.48
Castro et al., 1995	Temperate forest	42° 30′N, 72°10′W	0	0.72	1.00
Castro et al., 1995	Temperate forest	42° 30′N, 72°10′W	5	1.92	1.53
Castro et al., 1995	Temperate forest	42° 30′N, 72°10′W	10	3.6	2.00
Castro et al., 1995	Temperate forest	42° 30′N, 72°10′W	20	4.8	2.33
Whalen and Reeburgh, 1996	Boreal forest	64°N 148°W	10	2.78	2.00
Whalen and Reeburgh, 1996	Boreal forest	64°N 148°W	20	5.56	3.00
Whalen and Reeburgh, 1996	Boreal forest	64°N 148°W	30	4.86	2.75
Whalen and Reeburgh, 1996	Boreal forest	64°N 148°W	40	1.25	1.45
Dasselaar et al., 1998	Grassland	52°09′N, 5°5′E	5	0	1.00
Dasselaar et al., 1998	Grassland	52°09′N, 5°5′E	10	1.8	2.00
Dasselaar et al., 1998	Grassland	52°09′N, 5°5′E	15	3.8	3.11
Dasselaar et al., 1998	Grassland	52°09′N, 5°5′E	20	4.2	3.33
Dasselaar et al., 1998	Grassland	52°09′N, 5°5′E	25	5	3.78
Del Grosso et al., 2000	Grassland	40°47′N, 104°36′W	-7	0.2	0.3
Del Grosso et al., 2000	Grassland	40°47′N, 104°36′W	-4	0.3	0.4
Del Grosso et al., 2000	Grassland	40°47′N, 104°36′W	-3	0.5	0.7
Del Grosso et al., 2000	Grassland	40°47′N, 104°36′W	0	0.7	1.00
Bradford et al., 2001	Temperate forest	51°N, 2°W	3	1.79	1.61
Bradford et al., 2001	Temperate forest	51°N, 2°W	6	2.08	1.71
Bradford et al., 2001	Temperate forest	51°N, 2°W	9	2.50	1.86
Bradford et al., 2001	Temperate forest	51°N, 2°W	12	2.92	2.00
Bradford et al., 2001	Temperate forest	51°N, 2°W	15	3.33	2.14
Lau et al., 2015	Tundra	79°24′N, 90°45′W	4	0.25	2.00
Lau et al., 2015	Tundra	79°24′N, 90°45′W	10	0.75	4.00

Table A2.3 Observations used to construct r_N based on the response of the CH_4 soil uptake to the addition of nitrogen in different ecosystems.

Author	Ecosystem	Location	N added (kg N ha^{-1} y^{-1})	CH_4 oxidation reduction (%)
Steudler et al., 1989	Temperate forest	43°31′N,72°11′W	37	15
Steudler et al., 1989	Temperate forest	43°31′N,72°11′W	120	33
Nesbit and Breitenbeck, 1992	Temperate forest	31°N, 92°W	50	4
Hansen et al., 1993	Agricultural field	63°00′N,8°88′E	140	50
Schnell and King, 1994	Laboratory experiment		14.08	6
Crill et al., 1994	Peatland	62°51′ N,30°53′E	100	50
Neff et al.,1994	Alpine soils	40°01′N,105°32′W	250	52
Kightley et al., 1995	Landfill cover soil	lab soil	100	64
Sitaula et al., 1995	Temperate forest	58°49′N,8°32′E	30	15
Sitaula et al., 1995	Temperate forest	58°49′N,8°32′E	90	38
Hütsch et.al., 1996	Temperate arable soils	51°N,10°E	50	15.6
Steinkamp et al.,2001	Temperate forest	48°18′N 11°E	150	30
Veldkamp et al., 2001	Tropical pasture	10°20′N, 84°55′W	300	75
Gulledge et al., 1997	Temperate forest	42°30'N, 72°12' W	150	49
Zhang et al., 2008	Temperate forest	23°10′N, 112°10′E	100	14
Zhang et al., 2008	Temperate forest	23°10′N, 112°10′E	150	32
Jassal et al., 2011	Temperate forest	49°52′N, 125°20′W	200	50
Fender, 2012	Temperate forest	51°04' N, 10°30' E	200	86
Fang et al., 2014	Alpine meadow	37°37′ N, 101°19′ E	10	1.9
Fang et al., 2014	Alpine meadow	37°37′ N, 101°19′ E	20	8.6
Fang et al., 2014	Alpine meadow	37°37′ N, 101°19′ E	40	18.5

Appendix B

B1. Global driving data used to force the model

All datasets were re-gridded onto a 1°x1° grid. Maps for time-varying variables show the average for the period 1990-2009. The reference and link for each dataset are found at the end of this appendix.

Part 1: Time constant data

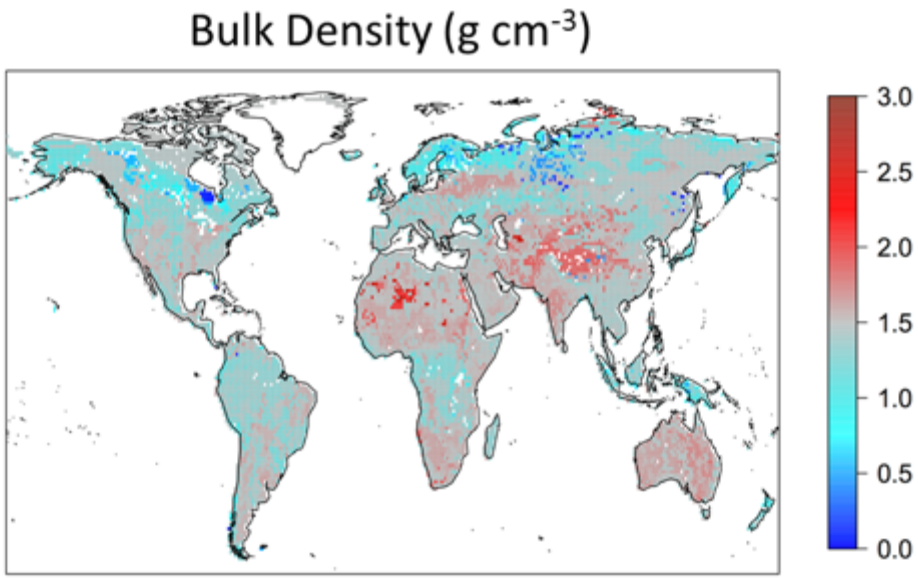

Figure B1.1 Global gridded mean bulk density (g cm^{-3}) (Shangguan et al., 2014).

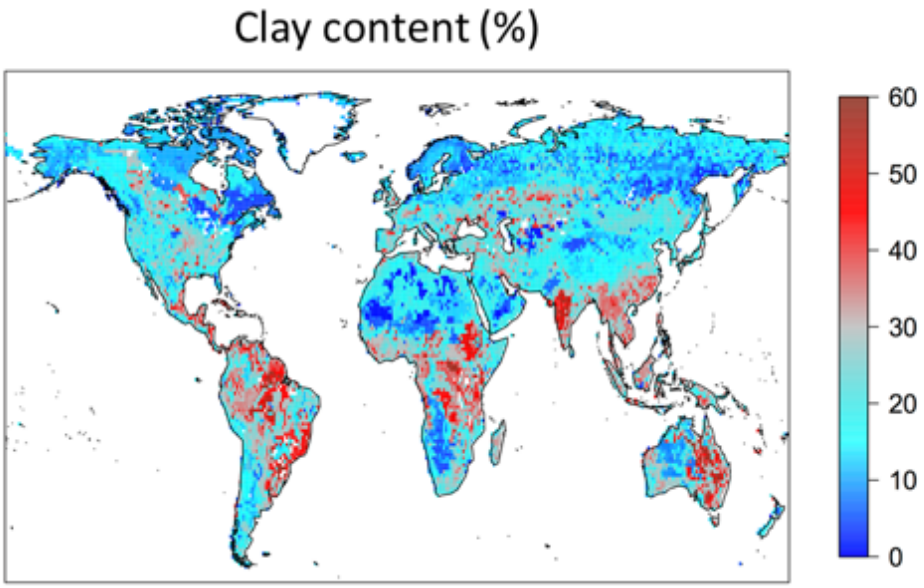

Figure B1.2 Global gridded mean clay content (%) (Shangguan et al., 2014).

Part 2: Time-varying data

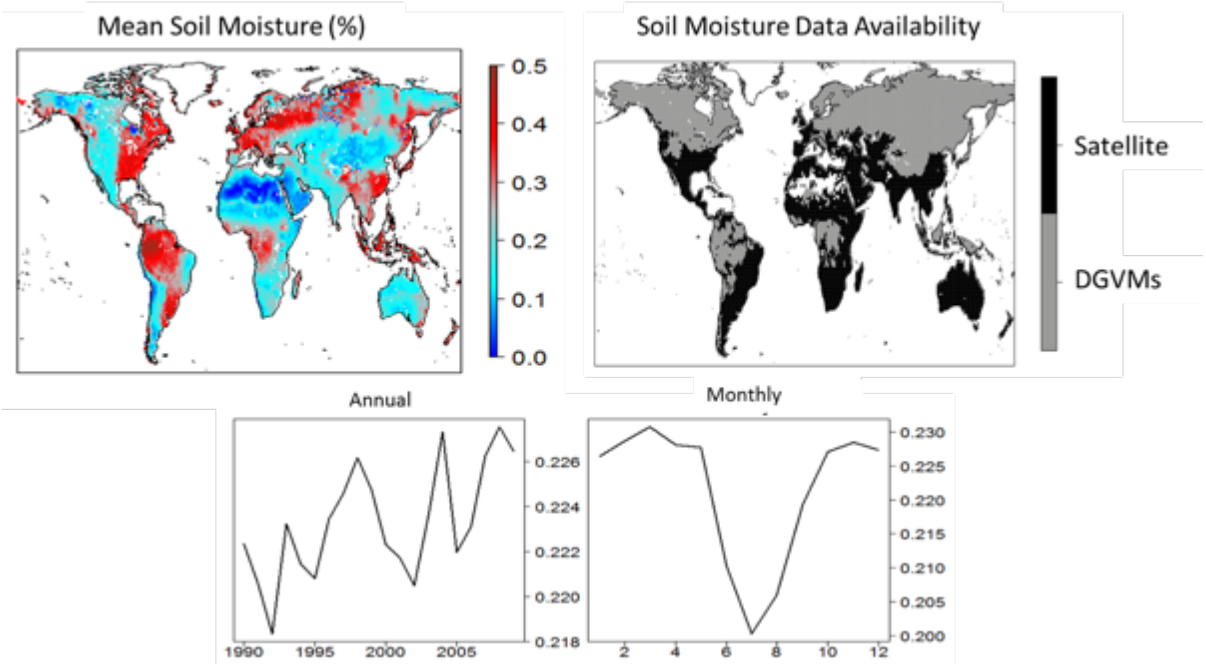

Figure B1.3 Mean soil moisture (%) as (top, left) global gridded mean, (bottom, left) annual mean and (bottom, right) monthly mean, from Dorigo et al. (2011). Gaps were filled using model data from TRENDY (Sitch et al. (2015)) (upper, right).

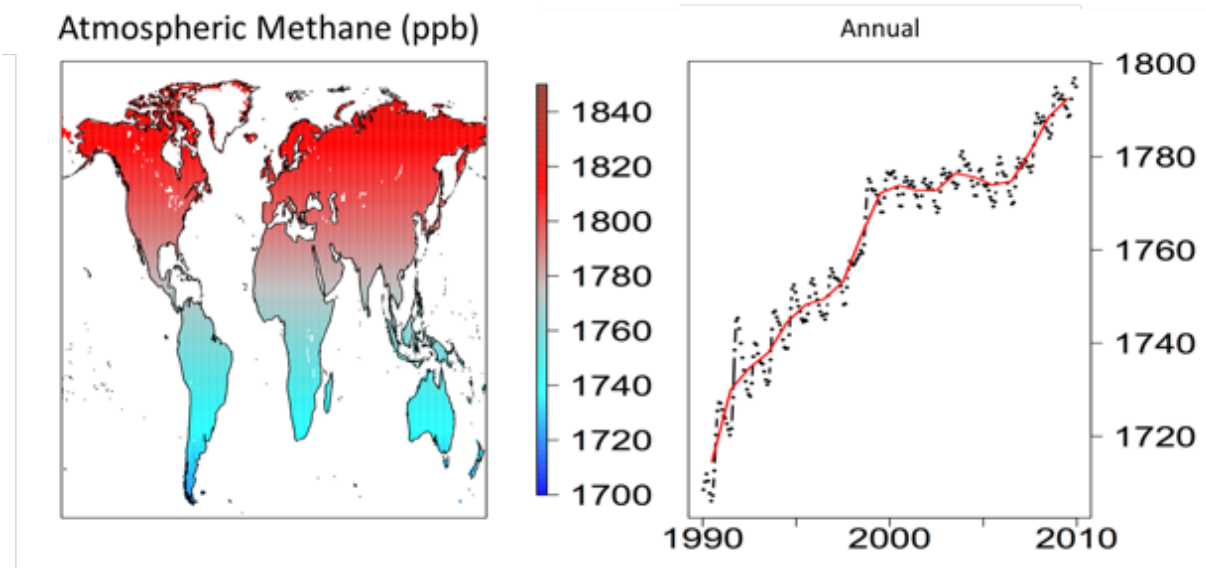

Figure B1.4 Atmospheric methane concentration (ppb) over 1990-2009 as (left) gridded mean and (right) annual mean (Rigby et al., 2008).

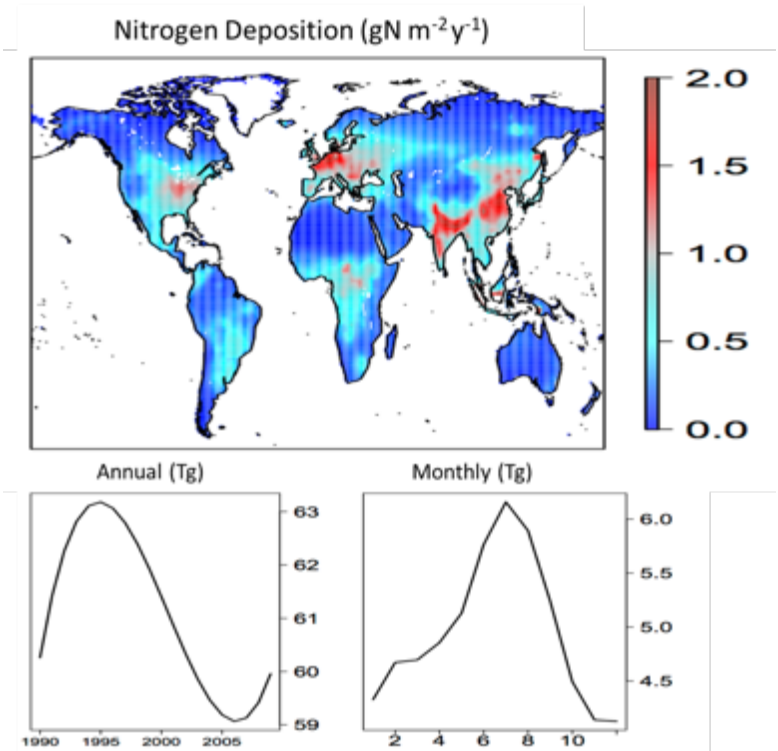

Figure B1.5 Mean soil nitrogen deposition (gN m^{-2} y^{-1}) over 1990-2009 as (top) global gridded mean, (bottom, left) annual mean and (bottom, right) monthly mean (Lamarque et al., 2013)

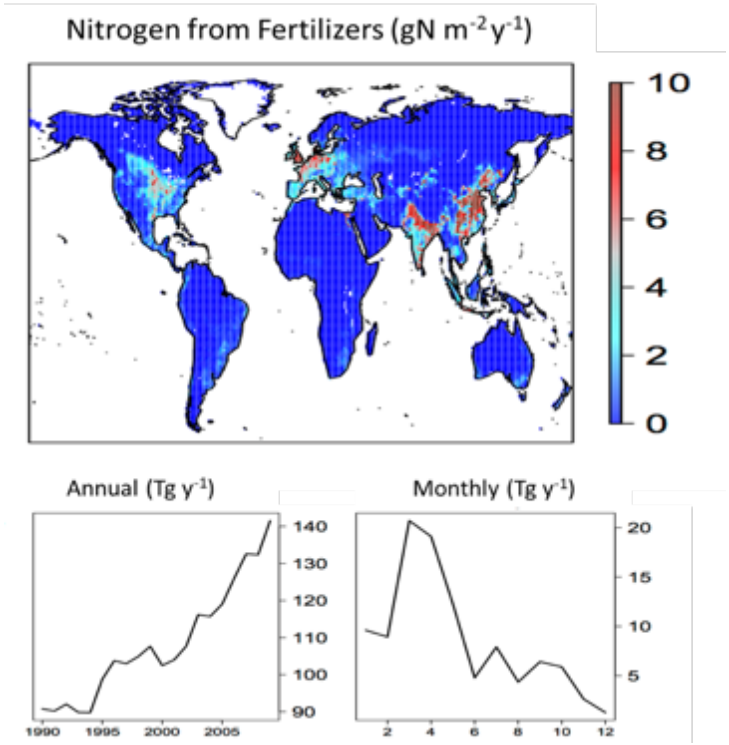

Figure B1.6 Mean soil nitrogen input from fertilizers (gN m^{-2} y^{-1}) over 1990-2009. (Top) global gridded mean, (bottom, left) annual mean and (bottom, right) monthly mean (Nischina et al., 2017).

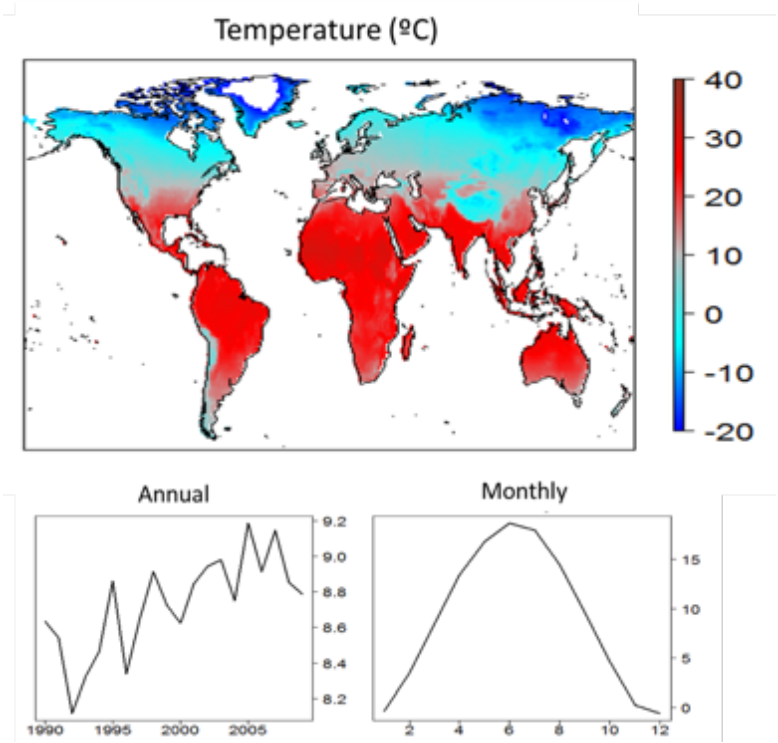

Figure B1.7 Mean surface temperature (ºC) over 1990-2009 as (top) global gridded mean, (bottom, left) annual mean and (bottom, right) monthly mean (CRU3.1, Harris et al., 2014).

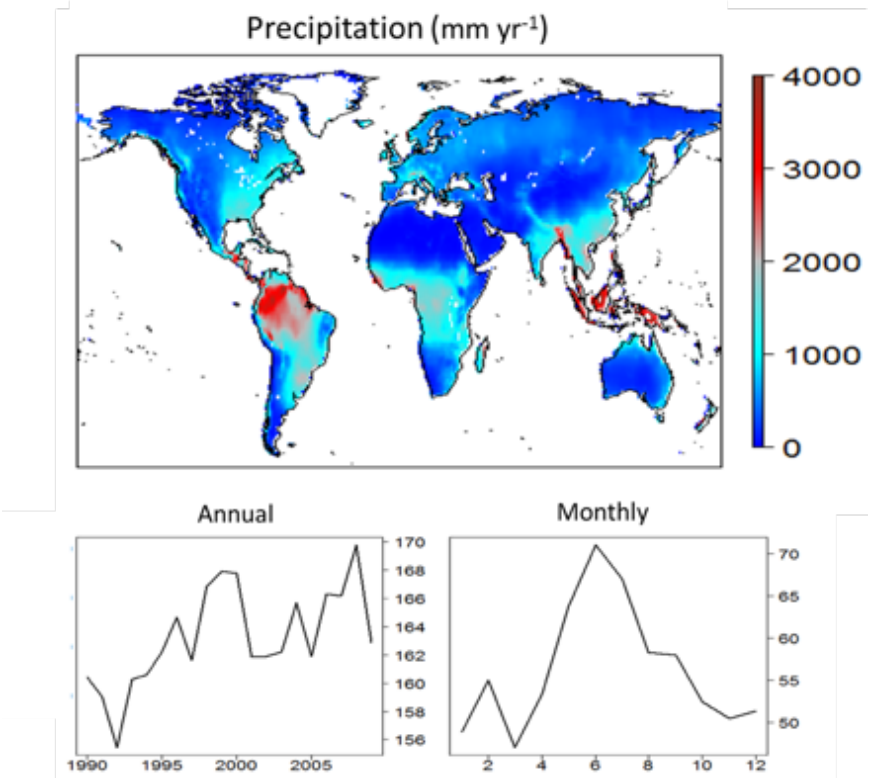

Figure B1.8 Mean precipitation (mm yr^{-1}) over 1990-2009 as (top) global gridded mean, (bottom, left) annual mean and (bottom, right) monthly mean. *Used to force R99.* (CRU3.1, Harris et al., 2014).

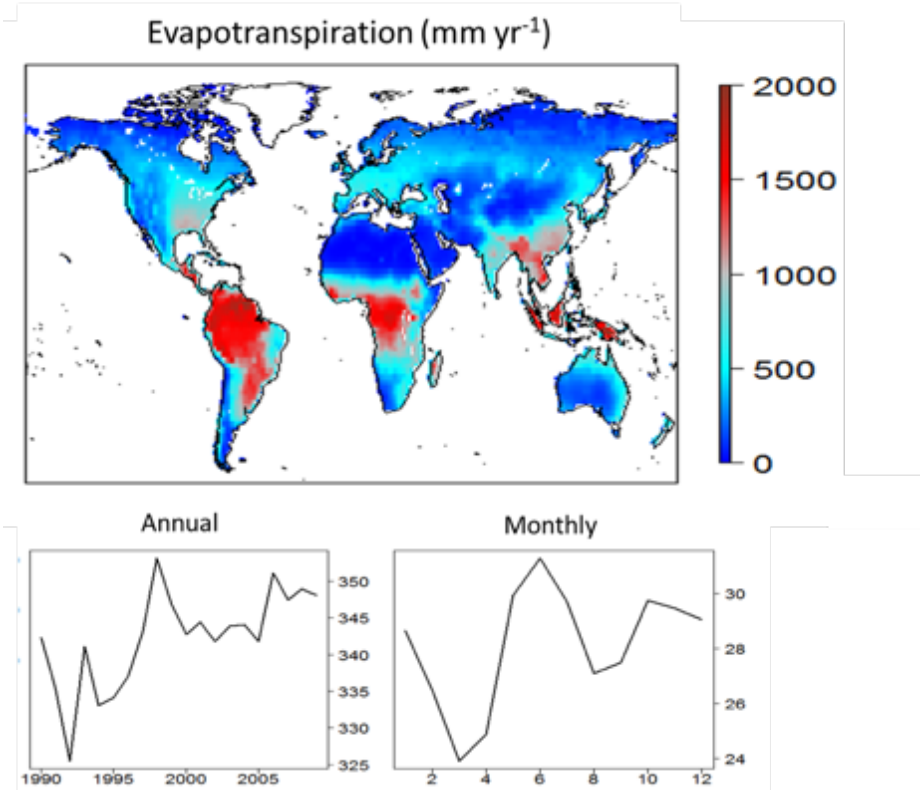

Figure B1.9 Mean evapotranspiration (mm yr^{-1}) over 1990-2009 as (top) global gridded mean, (bottom, left) annual mean and (bottom, right) monthly mean. *Used to force R99.* (TRENDY; Sitch et al., 2015).

B1.10 Vegetation mask

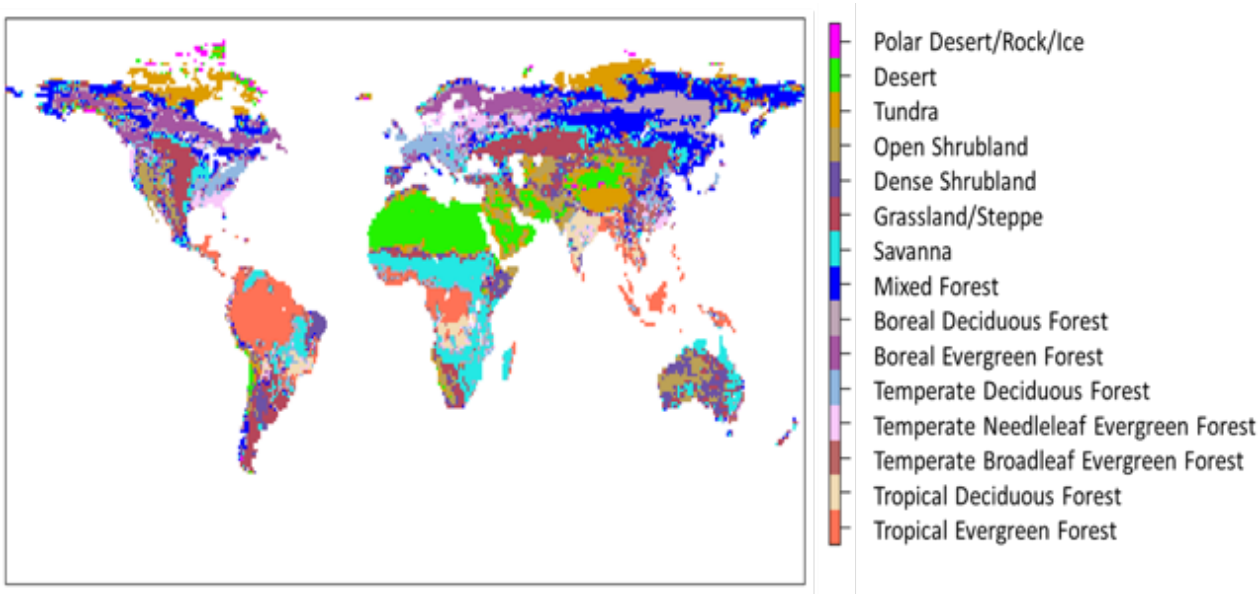

Figure B1.10 Vegetation distribution mask (Ramankutty and Foley 1999).

Data availability

All the data sets used to run MeMo, C07 and R99 are available from the following sources:

- Temperature and Precipitation: https://crudata.uea.ac.uk/cru/data/hrg/
- Vegetation mask: https://nelson.wisc.edu/sage/data-and-models/global-potential-vegetation/index.php
- Soil Moisture (Satellite): http://www.esa-soilmoisture-cci.org
- Soil Moisture (TRENDY): http://www-lscedods.cea.fr/invsat/RECCAP/
- Nitrogen deposition:
  1) https://www.isimip.org/gettingstarted/downloading-input-data/
  2)https://www.isimip.org/gettingstarted/details/24/
- Nitrogen input from fertilizers: https://www.earth-syst-sci-data.net/9/149/2017/
- Clay Content and bulk density: http://globalchange.bnu.edu.cn

Appendix C

C.1 Relative change in uptake (to the optimum) by ecosystem at different temperatures

Table C1.1 Mean distance (in °C) from the optimum temperature (28ºC) for the uptake by ecosystem. The change in uptake was calculated using r_T from MeMo v1.0, estimating the relative change of uptake (%) between the late 20th century (1980-2015) uptake value and when temperature increases 2ºC (T+2), 5 ºC (T+5) and 10 ºC (T+10) for each ecosystem. * detonates ecosystems that could have less uptake due to high temperatures.

Ecosystem	Distance to optimum (ºC)	Relative change in uptake (%)		
		T+2	T+5	T+10
Tropical Evergreen Forest	-2.3±1.9	104%	96%*	87%*
Tropical Deciduous Forest	-3.7±2.7	105%	98%*	91%*
Temperate Broadleaf Evergreen Forest	-6.3±4.8	106%	101%	98%*
Temperate Needleleaf Evergreen Forest	-13.5±7.8	107%	106%	111%
Temperate Deciduous Forest	-15.0±6.3	108%	107%	115%
Boreal Evergreen Forest	-23.1±8.7	144%	209%	260%
Boreal Deciduous Forest	-24.1±12.4	184%	543%	2133%
Mixed Forest	-30.2±8.5	207%	605%	3713%
Savanna	-11.3±12.8	129%	223%	1065%
Dense Shrubland	-10.2±8.9	131%	228%	1067%
Open Shrubland	-13.5±10.8	114%	133%	230%
Tundra	-32.2±12.0	124%	202%	940%

C1.2 Frozen area extension

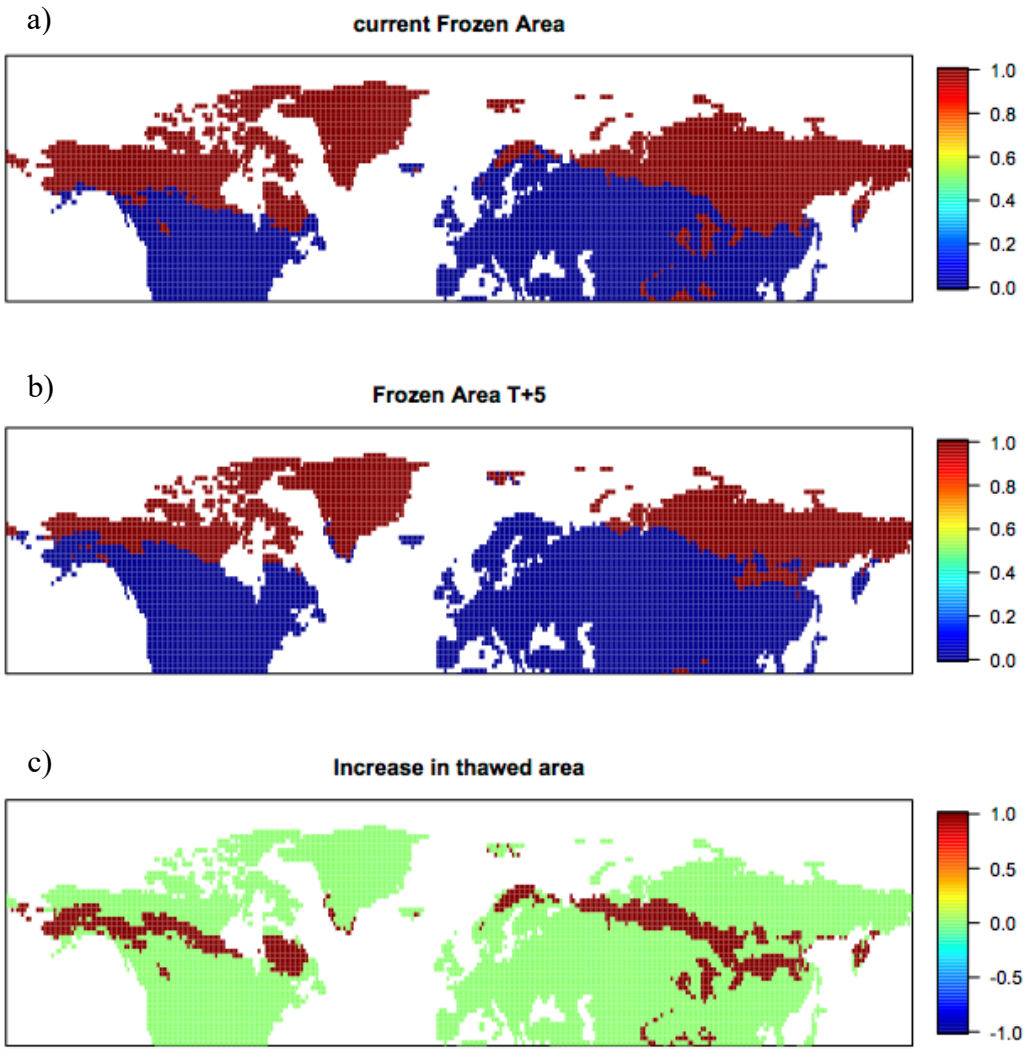

Figure C1.2 Change in the frozen area raising 5°C. a) late 20th century (1980-2015) frozen area extension. b) The frozen area when temperature increases 5°C respect to late 20th century. c) change in frozen area (red zones: defrosted areas). Frozen areas were considered regions with annual mean temperatures below -5ºC

C1.3 Soil Methanotrophy active season

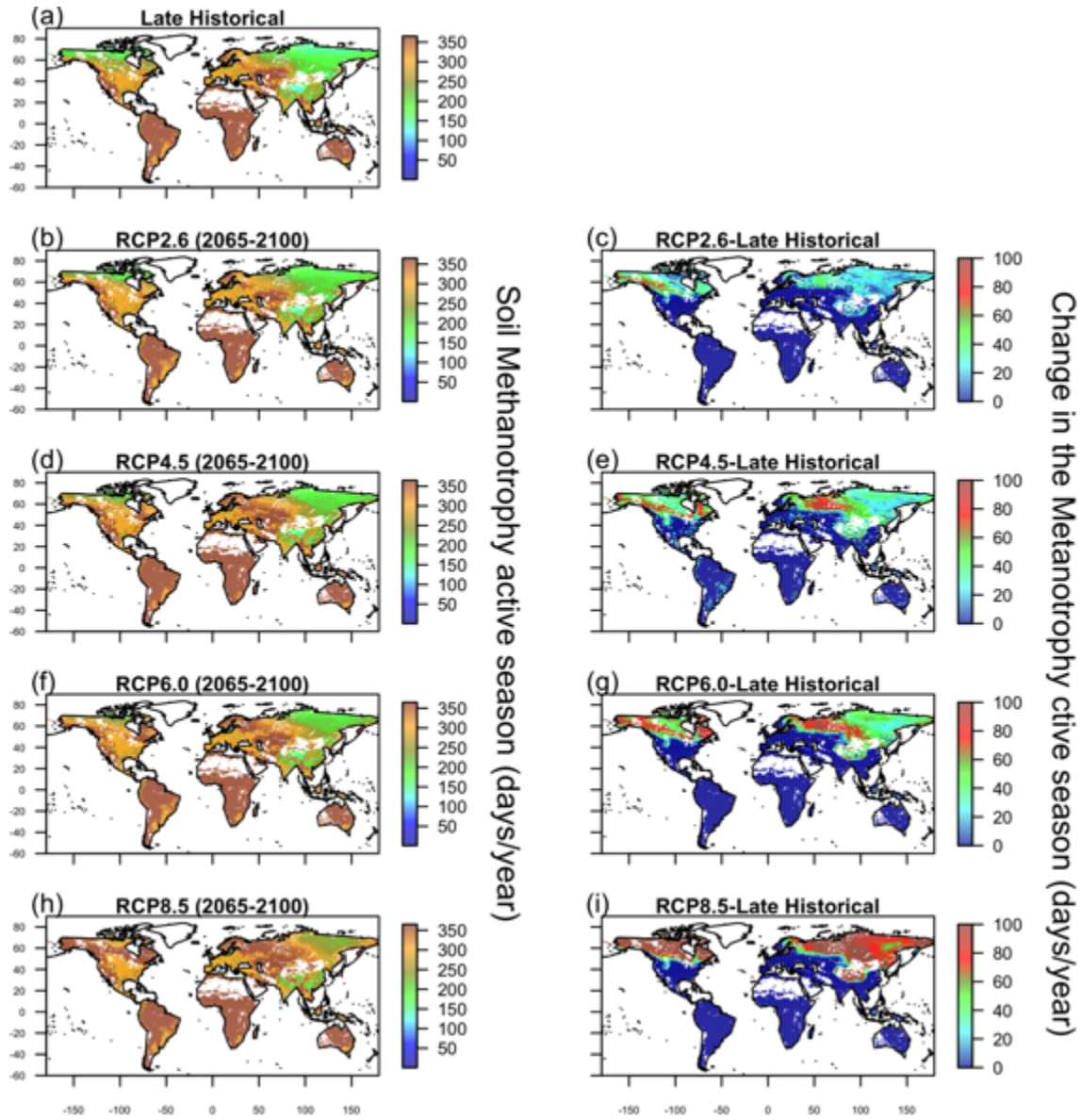

Figure C1.3 Mean number of days per year during which soil methanotrophy is active for (a) late historical period (1980-2015) and late 21st century (2065-2100) in (b) RCP2.6, (d) RCP4.5, (f) RCP6.0 and (h) RCP8.5. The differences in number of active days between the late historical period and each RCP scenario are shown in panels (c), (e), (g) and (i).

C2.1 N inputs and cropland area fraction

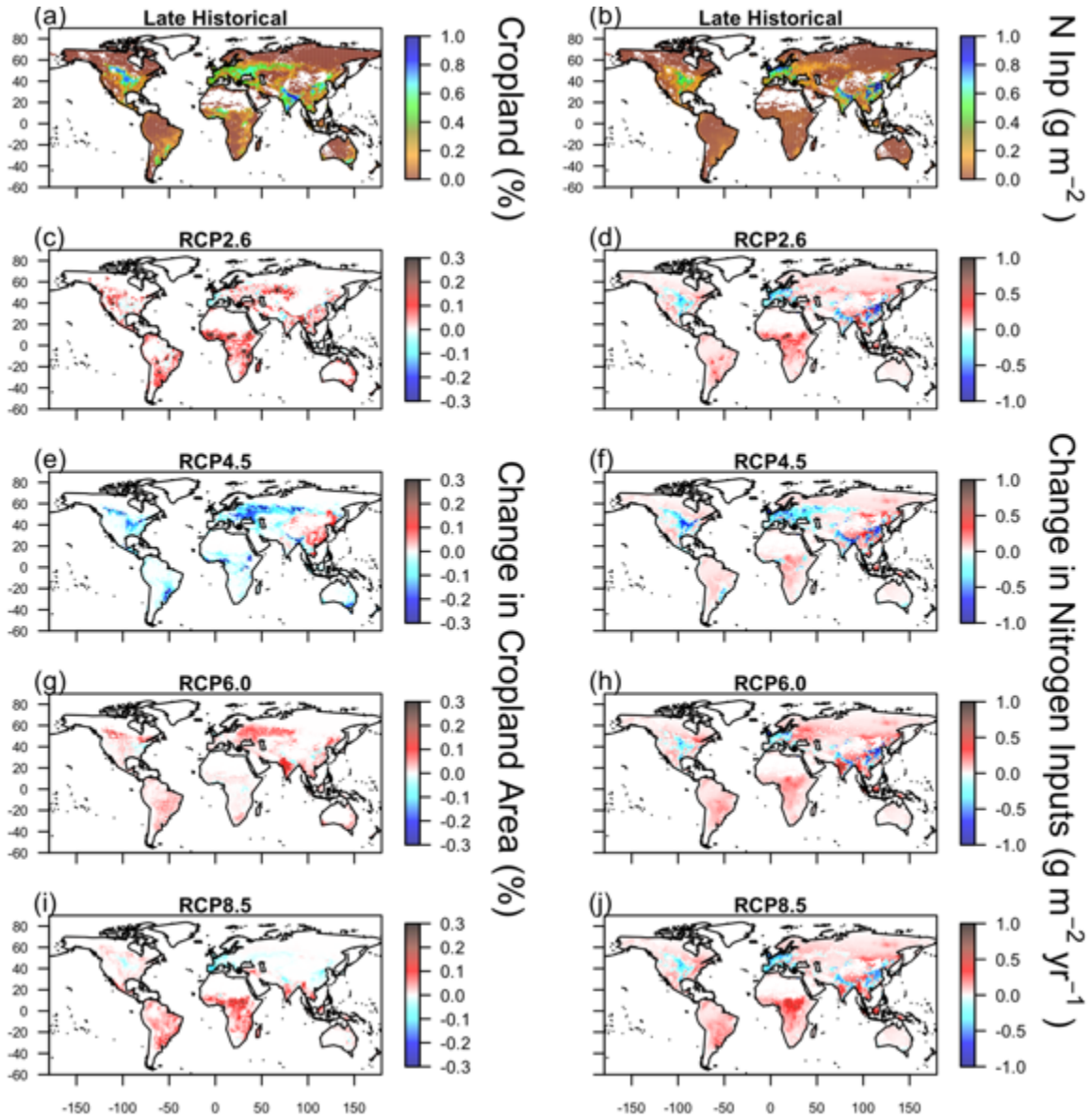

Figure C2.1 Global (a) cropland area and (b) mean N input via atmospheric N deposition and application of fertilizer for the late historical period (1980 to 2015). Differences in cropland area (expressed as % change) between the late historical (a) and the period 2065 to 2100 are shown for (c) RCP2.6, (e) RCP4.5, (g) RCP6.0, and (i) RCP8.5. Differences in N input via atmospheric N deposition and fertilizer application (both expressed in g N m^{-2} yr^{-1}) between the late historical (b) and the period 2065 to 2100 are shown for (d) RCP2.6, (f) RCP4.5, (h) RCP6.0 and (j) RCP8.5.

C3.1 Soil moisture change

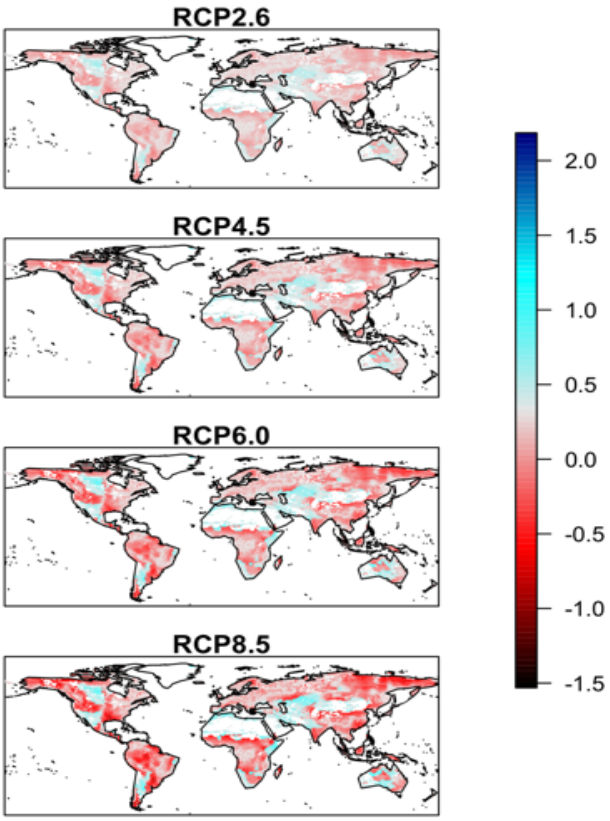

Figure C3.1 Annual soil moisture changes for the four RCP´s (2065-2100). (Taylor, 2012)

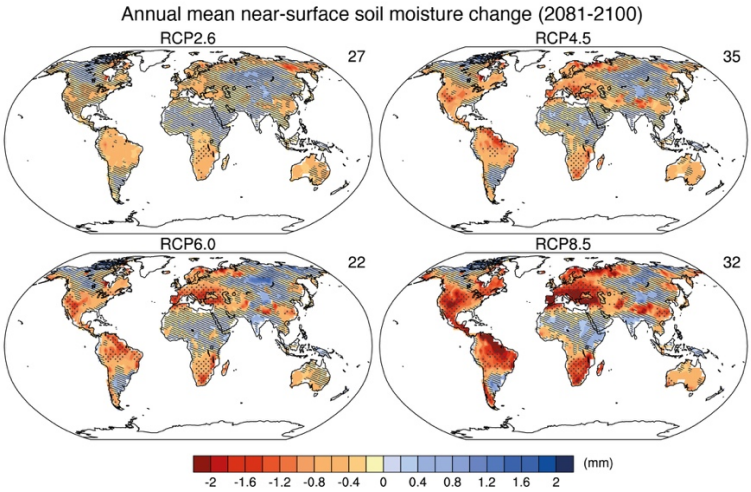

Figure C3.2 Annual mean soil moisture change (2081-2100). Figure 12.23 of the IPCC AR5 report

C3.3 Soil moisture qualitative effect over uptake

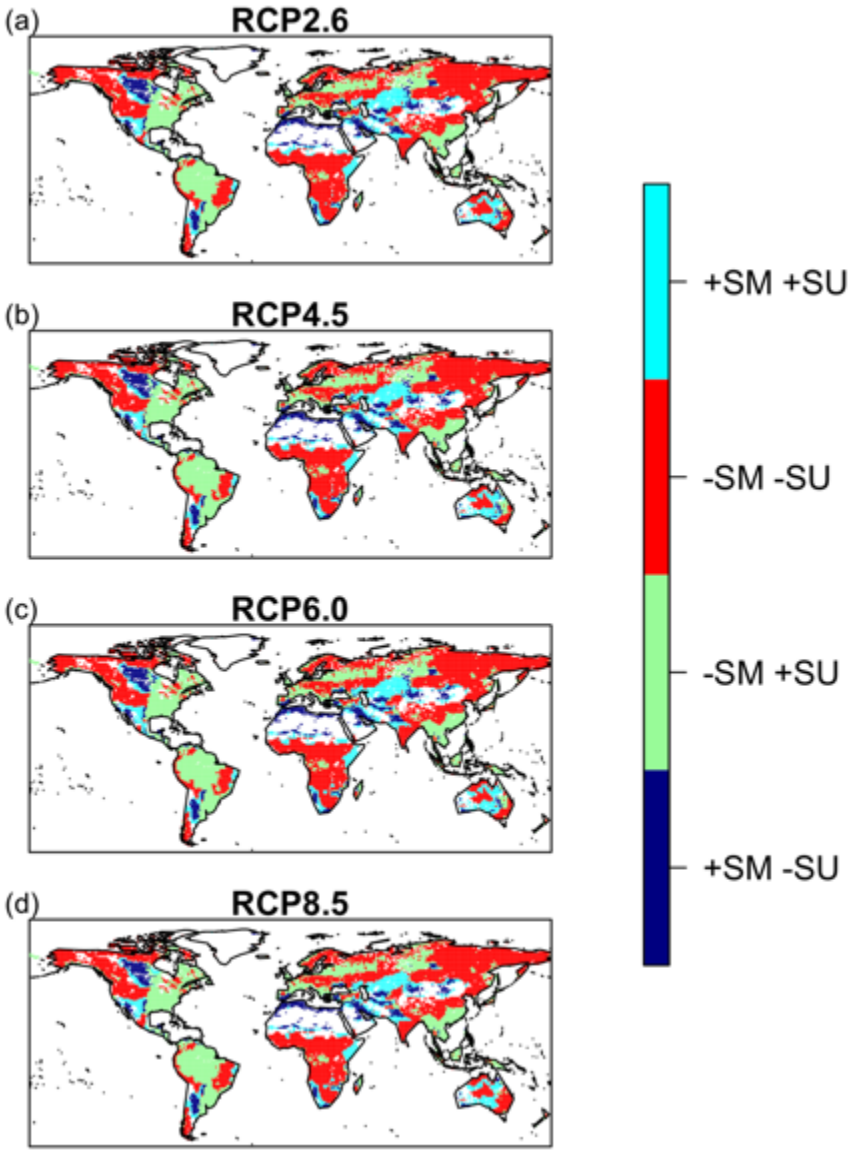

Figure C3.3 Qualitative assessment of increases (+) and decreases (-) in SM and soil uptake of atmospheric CH_4 (SU) across (a) RCP2.6, (b) RCP4.5, (c) RCP6.0 and (d) RCP8.0, relative to late historical period (1980-2015). The four possible combinations of change are: (i) an increase in both SM and CH_4 uptake (light blue); (ii) a decrease in both SM and CH_4 uptake (red); (iii) a decrease in SM and increase in CH_4 uptake (green); and (iv) an increase in SM and decrease in CH_4 uptake (dark blue).